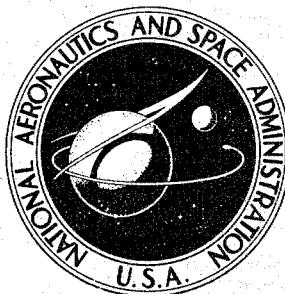


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**THE DEVELOPMENT OF THERMALLY
STABLE ADHESIVES FOR TITANIUM ALLOY
AND BORON COMPOSITE STRUCTURES**

*by R. W. Vaughan, R. J. Jones,
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16. Abstract This final report describes the work performed to develop thermally stable adhesives for bonding titanium alloy and boron composite substrates. TRW A-type polyimide technology was employed as a basis for a series of adhesive formulations evaluated for bonding titanium alloy 6Al4V and boron/polyimide composites. It was shown that copolymeric blends of an A-type polyimide and amide-imide resin provided superior adhesive properties at elevated and cryogenic temperatures than state-of-the-art adhesives. Data are presented for the most promising adhesive selected during this program on long term elevated and cryogenic aging of bonded assemblies and for stress-rupture tests at elevated temperature.					
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FOREWORD

This document is the final report for the work performed during the period 7 October 1969 through 7 September 1970 by TRW Systems for the National Aeronautics and Space Administration, Langley Research Center, under Contract NAS1-9532. The report covers Tasks I, II and III of the program which involves Development of Thermally Stable Adhesives for Titanium Alloy and Boron Composite Structures. Pursuant to a contractual change received on the 19 August 1970 a final report for additional Tasks IV, V, VI and VII will be prepared in September 1971. These additional Tasks extend the scope of work to include graphite-polyimide composites as substrates and to provide autoclave processability for the adhesives.

This work was conducted under the technical direction of Mr. Robert Baucom of the Langley Research Center, Hampton, Virginia.

The Chemical Technology and Chemical Research and Services Departments of the Chemistry and Chemical Engineering Laboratory, Science and Technology Division were responsible for the work performed on this program. Dr. E. A. Burns, Manager, Chemical Research and Services Department provided overall program supervision and Mr. R. W. Vaughan, Plastics Technology Section, was Program Manager. Major technical contributions throughout the program were provided by Mr. J. F. Creedon, adhesive formulary, processing and evaluation; Dr. R. J. Jones, polymer synthesis; Mr. J. W. Goodman, structural analysis and Mr. G. Fukumoto, structural testing. Acknowledgment is made of the technical assistance provided during the program by the following TRW Systems personnel.

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THE DEVELOPMENT OF THERMALLY STABLE ADHESIVES FOR TITANIUM ALLOY AND BORON COMPOSITE STRUCTURES

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TRW SYSTEMS

1. INTRODUCTION AND SUMMARY

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Langley Research Center under Contract NAS1-9532 during the period 7 October 1969 through 7 September 1970. The objective of this program was to develop an advanced thermally stable adhesive, based upon a TRW "A"-type polymer, for bonding titanium alloy and boron composite substrates.

Key basic technology upon which these developmental studies were based was established during a previous NASA Contract NAS3-7949 (Reference 1) during which TRW developed a new polyimide resin system which offered distinct advantages in processing over other available high performance polymers cured by a condensation reaction. The new resin system, termed "A"-type polyimide, is formed by a unique addition-type curing mechanism called pyrolytic polymerization. In-depth polymer studies that have provided substantial background for developmental studies in this program were performed under NASA Contract NAS3-12412 (Reference 2).

During the program discussed in this report, specific "A"-type formulations containing both single and mixed diamines were synthesized and evaluated as constituents for adhesive compounds. From these resin screening studies, one outstanding formulation was identified. Further modifications to this resin formulation and the use of additives were studied in order to obtain good adhesion to titanium alloy substrates. The success of this program is attributed to a copolymeric blend of the

"A"-type polyimide and a commercial amide-imide resin (Amoco AI-1137) which was identified as providing adhesive properties at 600°F and after iso-thermal aging at 600°F higher than state-of-the-art adhesives. Detailed mechanical testing was performed on bonded assemblies produced with this adhesive. These studies established design parameters under various use conditions such as long term elevated and cryogenic temperature exposure and long term stressed conditioning.

This report is divided into three principle sections devoted to the description of work performed in the three consecutive program tasks:

TASK I - Polymer Synthesis and Characterization

TASK II - Preliminary Adhesive Development and Evaluation Studies

TASK III - Detailed Evaluation of Selected Polyimide Adhesive Systems

A brief structural analysis-study of data generated during this program showed that the shear strength developed by the selected adhesive in balanced assemblies with mixed substrates was greater than the shear strength of boron polyimide composites. Conclusions were drawn from the results of this program and are listed together with recommendations for related studies which warrant further investigation. Significant experimental details supplementing the narrative of this report are provided in the appendices.

2. POLYMER SYNTHESIS AND CHARACTERIZATION STUDIES

In order to investigate improved "A"-type polyimide resin formulations suitable for development of a superior adhesive candidate, six key ingredients were selected which had demonstrated specific attributes for improving thermo-oxidative stability and/or processability of the polymer family. The monomers selected are given in Table I along with an abbreviation code employed throughout the remainder of this report. The six ingredients either were washed with solvent or recrystallized to give monomers of a melting range of 1-3°C.

These monomers were utilized in selected resin combinations and formulated molecular weights as given in Table II. The prepolymers at the indicated FMW were prepared as amic-acid (A-A) varnishes in dimethyl formamide (DMF) at a 40% w/w solids loading according to the procedure described in Appendix A. The varnish viscosities obtained compare favorably with a 190-200 cps (25°C) viscosity range routinely observed for a commercially available TRW "A"-type polyimide formulation designated P13N.

TABLE I.
MONOMERS SELECTED FOR UNDERTAKING RESIN STUDIES

Monomer	Code
Nadic anhydride	NA
Methylene dianiline	MDA
<u>meta</u> -Phenylene diamine	MPD
Sulfo dianiline	SDA
Benzophenone tetracarboxylic acid dianhydride	BTDA
Pyromellitic dianhydride	PMDA

Screening of these resin systems then was performed by characterization of the physical properties for the three resin forms, i.e. amic-acid, polyimide prepolymer and cured polyimide resin and by determination of shear strength provided by them in titanium-to-titanium bonded lap shear joints. Discussion of these screening studies is provided in the following narrative.

TABLE II.
"A"-TYPE FORMULATIONS

Formulation	Formulated Molecular Weight (FMW)	Brookfield Viscosity (cps)	Temperature (°C)
NA/MDA/BTDA	1150	138	24
NA/MPD/BTDA	1100	235	24
NA/MDA/PMDA	1000	154	25
NA/90MDA:10SDA/BTDA	1150	188	24
NA/90MPD:10SDA/BTDA	1100	312	24
NA/90MDA:10SDA/PMDA	1000	215	24
MA/MPD /BTDA	1300	633	24

2.1 CHARACTERIZATION OF PHYSICAL PROPERTIES

Each experimental varnish was subjected to structural analysis by infrared spectroscopy and gave similar spectra to the representative one given for NA/90MPD:10SDA/BTDA (1100 FMW) in Figure 1. The absorption in $1640 - 1720 \text{ cm}^{-1}$ region is specific for the desired A-A prepolymer linkage and appeared in all six spectra. Other definitive bands of importance are at 1260 cm^{-1} (DMF) and $2860-3000 \text{ cm}^{-1}$ (nadic). After it was established that the varnishes contained the desired A-A prepolymer, the resin was isolated and converted to imidized prepolymer powders by the method described in Appendix A.

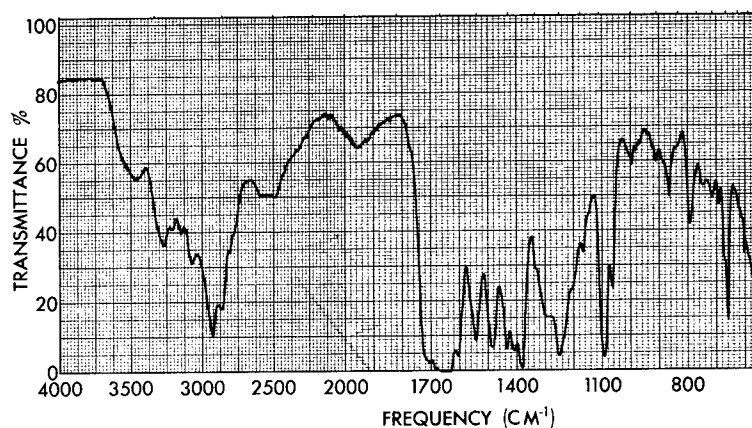


Figure 1. Infrared Spectrum of 1100 FMW NA/90MPD:10SDA/BTDA Amic-Acid Varnish.(Smear on NaCl Plate)

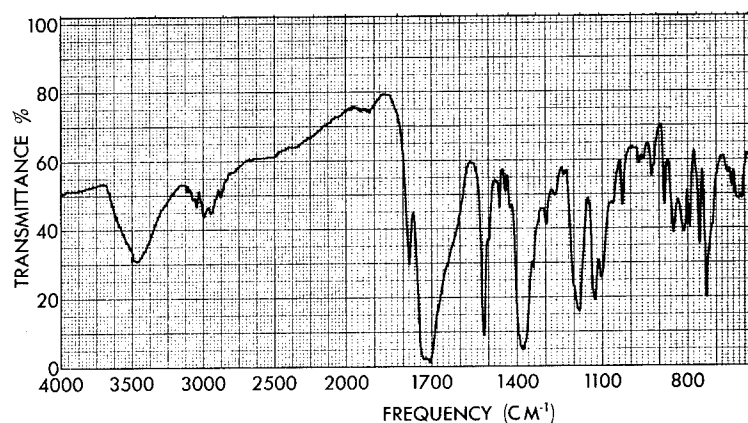


Figure 2. Infrared Spectrum of 1000 FMW NA/90MDA:10SDA/PMDA Imidized Prepolymer. Concentration: 4.9 mg/g KBr

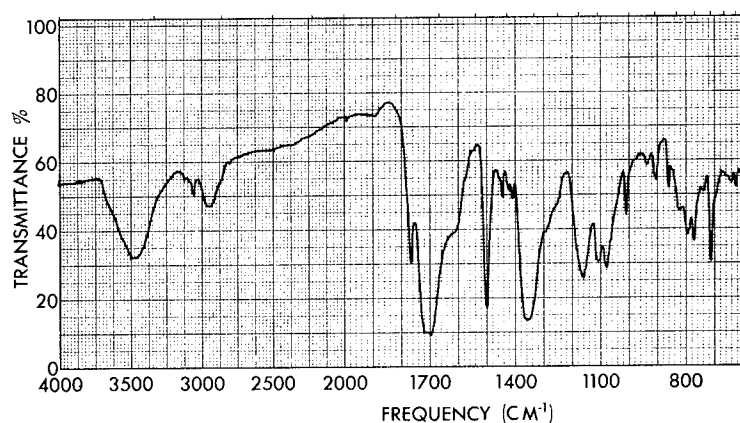


Figure 3. Infrared Spectrum of 1000 FMW NA/MDA/PMDA Cured Polymer. Concentration: 6.0 mg/g KBr

The six resin powders were checked for imidization by infrared analysis. A typical representative spectra is given in Figure 2 for NA/90MDA:10SDA/PMDA (1000 FMW). In this spectra the absorptions in the 1700-1780 cm^{-1} region are specific for "A"-type imide linkages. Attention is called also to the disappearance of A-A character below 1700 cm^{-1} and strong DMF absorption at 1260 cm^{-1} (See Figure 1). The nadic group still is present as indicated by absorption bands in the 2900-3000 cm^{-1} region. The imidized prepolymer powders were molded under conditions adequate to give complete cure and consolidation. The results of the molding study are given in Table III.

TABLE III.
A-TYPE POLYIMIDE CURING STUDIES

Formulation FMW	FMW	Dwell Time Min	psig	Temp (°F)	Cure Time (Min)	Barcol	Observations
NA/90MPD:10SDA/BTDA	1000	0	400	555	30	52	High Flow
NA/90MDA:10SDA/BTDA	1150	5	400	559	30	43	High Flow
NA/MDA/BTDA	1150	5	400	550	30	43	Some Flow
NA/MPD/BTDA	1100	5	400	572	30	55	Some Flow
NA/MDA/PMDA	1000	0	500	611	30	45	Some Flow
NA/90MDA:10SDA/BTDA	1150	0	500	619	30	42	Very Little Flow

Because each formulation gave visual evidence of flow and good consolidation (high Barcol hardness), it was recommended that the temperatures given in Table III be employed for curing lap shear specimens of each specific resin modification.

The cured plugs were ground to a fine ($\sim 5\mu$) powder and screened for indications of desired structure by infrared analysis. The spectra shown in Figure 3 for NA/MDA/PMDA (1000 FMW) is representative for all modifications. The polyimide backbone remained intact during cure as indicated by the absorption bands in the 1700-1780 cm^{-1} region (refer to Figure 2). A hydrocarbon species related to nadic still is present as is shown by the absorptions at 2900-3000 cm^{-1} which also was present for the prepolymer (Figure 2).

The six cured "A"-type polyimide modifications were screened for thermal stability by TGA in nitrogen and air. The data obtained from runs on each material in nitrogen is given in Table IV. These data

show that excellent weight retention on exposure to nitrogen occurred for all formulations, particularly the two containing MPD and BTDA as the principle components.

TABLE IV.
TGA SCREENING ANALYSIS IN NITROGEN^{a)}

Formulation	FMW	Temperature Showing Indicated Weight °C				Char Yield @ 800°C
		Weight Loss, % w/w				% w/w
		10%	20%	30%	40%	
NA/90MPD:10SDA/BTDA	1100	460	520	580	650	55
NA/90MDA:10SDA/BTDA	1150	450	500	550	590	50
NA/MDA/BTDA	1150	430	480	520	560	52
NA/MPD/BTDA	1100	450	520	570	630	57
NA/MDA/PMDA	1000	430	460	510	550	48
NA/90MDA:10SDA/PMDA	1000	440	480	520	560	50

TGA screening in air data are summarized in Table V. As can be seen from Table V, the cured 1100 formulated molecular weight (FMW) compositions consisting of NA/MPD/BTDA and NA/90MPD:10SDA/BTDA demonstrated the greatest thermo-oxidative stability in air which paralleled the thermal stability data in nitrogen (Table IV).

TABLE V.
TGA SCREENING ANALYSIS IN AIR^{a)}

FORMULATIONS	FMW	TEMPERATURE AT WHICH INDICATED WEIGHT LOSS OCCURRED (°C)			
		WEIGHT LOSS, (%)			
		10%	20%	30%	40%
NA/90MPD:10SDA/BTDA	1100	430	500	520	530
NA/90MDA:10SDA/BTDA	1150	410	475	500	510
NA/MDA/BTDA	1150	380	450	475	485
NA/MPD/BTDA	1100	420	480	505	515
NA/MDA/PMDA	1000	370	430	460	470
NA/90MDA:10SDA/PMDA	1000	370	430	460	460

a) Determined on powder using a 3°C/Min scan rate and a 100cc/min nitrogen flow.

The potential of using Differential Scanning Colorimetry (DSC) for determining cured "A"-type polyimide melting points was assessed in this program. The melting point determinations employing a Perkin Elmer model DSC-1 apparatus proved to be futile for the amorphous "A"-type polyimide systems. In no instance was an endotherm or exotherm (indicative of a polymer melting point or finite transition point, respectively) observed up to 400°C. It was concluded that this analysis method was not applicable to the non-crystalline TRW "A"-type cured polyimide.

2.2 LAP SHEAR STRENGTH SCREENING

In order to obtain correlation between the candidate polymer's physical and mechanical characteristics, lap shear strength screening of these resins was performed. Standard five coupon pre-slotted panels of 6Al-4V titanium 0.040-inch thick (see Figure 4) were used throughout these studies. Preslotted panels were selected in preference to unslotted panels because they eliminated cutting metal adjacent to the bond line thus reducing heat and vibrational stress. Prior to commencing the actual polymer screening it was necessary to develop bonding techniques using the "A"-type polymers in order that accurate comparisons between systems could be made. Pasa-Jel 107 (Semco Inc.) was selected for pretreating the titanium faying surfaces because it is well proven industrially and has the advantage of being applied at room temperatures as a thickened paste (Reference 3 and 4) to the titanium finger panels. The bonding fixture used throughout this program (Figure 5) was designed to permit bond line thickness control either by spacers or by pressure control. Details of the lap shear specimen preparation studies and lap shear screening tests are provided in Appendix B.

As a result of these studies the procedure adopted for specimen preparation and evaluation was as follows.

The titanium specimens first were grit blasted followed by a Pasa-Jel 107 immersion for 15 minutes at ambient temperature. They then were rinsed in distilled water and dried for 3 minutes at 200°F in an air circulating oven. Immediately, a freshly prepared 40% solids BR-34 primer (diluted with dimethyl formamide) was brush applied on the faying surface. The coating was dried 30 minutes @ 220°F and cured 15 minutes @ 550°F. After

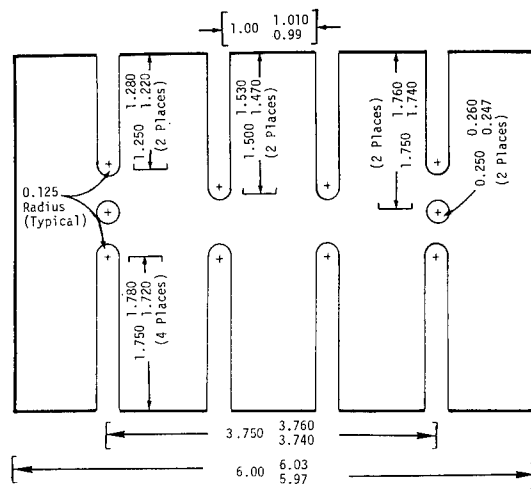


Figure 4. Lap Shear Specimens Slotted Panel

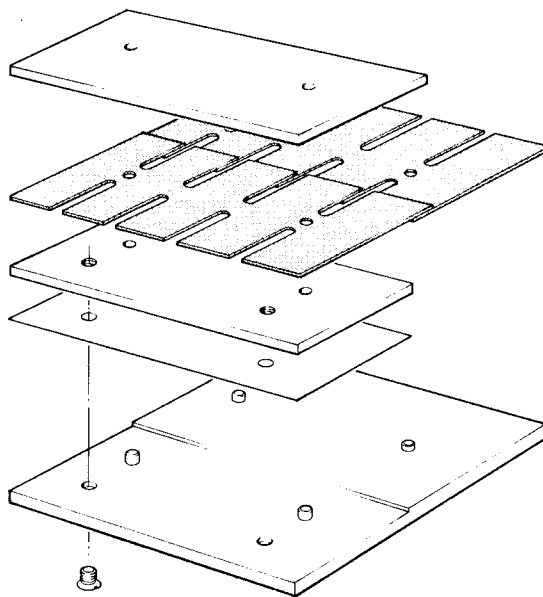


Figure 5. Lap Shear Specimens Bonding Jig

reaching ambient temperature, a knife coating of 81% w/w solids BR-34 primer was applied over the cured primer coats and dried for 30 minutes @ 220°F. A strip of candidate "A"-type amic-acid prepreg 6.5-inch long by 0.75-inch wide was laid on the 0.5-inch titanium faying surface in the bonding fixture. The second primed finger panel was placed in the press bonding fixture, a thermo-couple was placed between the third and fourth specimen, and the assembly was cured at 600°F under 200 psig pressure. The time-of-cure was measured starting from the time the recorder indicated the desired temperature. Time for the bonding assembly to reach 600°F was approximately 15 minutes thus providing an in situ imidization cycle.

After the specimens had been exposed to the desired cure cycle, the pressure was released and the bonding fixture was cooled on the bench to below 300°F before disassembly.

Two panels were fabricated for each resin system to provide 10 test coupons. Five were tested at ambient temperature and five were selected for 300 hours exposure at 600°F and tested at ambient temperature. It was noticed in the preliminary studies that there was some variation across the five specimens in each panel e.g., the two outer coupons typically tended to be lower in value than the three inner coupons. Therefore, in order to avoid weighted data, the specimens for aging were selected randomly. The panels that were to be exposed to 600°F for 300 hours were placed on two shelves in an air circulating oven. Since slight differences in aging temperature have an effect on shear strength, five thermo-couples were placed on each shelf and the temperatures were recorded. The temperature profile of the oven was judged to be non-critical.

The results of the screening tests on the six candidate adhesive polymer systems are reported in Table VI. From these results the NA/90MPD: 10SDA/BTDA (panels 70 & 71) and NA/MPD/BTDA (Panels 76 & 77) appear to provide the most thermally stable "A"-type polymer systems when utilized as adhesives based upon the following observations:

- Panels 70 & 71 provided the highest shear strength retention after aging
- Panels 76 and 77 provided the highest actual shear strengths after aging

- Panels 70 and 71 provided the second highest actual shear strengths after aging.

2.3 RESIN SELECTION

In both the TGA and lap shear strength screening evaluations it was clearly defined that the 1100 FMW NA/MPD/BTDA and 1100 FMW NA/90MPD:10SDA/BTDA systems were the best adhesives candidates for detailed assessment in Task II. TGA screening data in both nitrogen and air showed that the thermal stability of these two systems was better than the remaining four. These data were confirmed by the lap shear aging data wherein good shear strengths were obtained on specimens tested as molded and after aging for 300 hours at 600°F.

3. TASK II - PRELIMINARY ADHESIVE DEVELOPMENT AND EVALUATION STUDIES

Screening evaluations were performed through basic compounding studies and testing to determine the effects of co-reactive additives, fillers, thixotropic agents and reinforcement fabrics on the adhesive properties of the candidate "A"-type polyimide polymers selected in Task I. Surface treatments and adhesive primers were evaluated in conjunction with the above adhesive compounds.

3.1 TITANIUM SURFACE PREPARATION STUDIES

It is well established that titanium is notably more difficult to bond than aluminum and requires a pretreatment. Keith, Monroe and Martin (Reference 5) concluded that, at that time (1965), a phosphate fluoride pretreatment was the best. This involved treatment with an aqueous solution of nitric acid (14.2% w/v) and hydrofluoric acid (1.5% w/v) followed by rinsing and immersion in a solution of trisodium phosphate (5.0% w/v), potassium fluoride (2.0% w/v) and hydrofluoric acid (1.6% w/v).

Most references agree that the hydrofluoric acid in the pretreatment is the one most important chemical. Allen and Allen (Reference 6) obtained their best peel strength data by pretreatment immersion in either hydrofluoric acid or solutions of potassium fluoride in hydrofluoric acid and without hot water soaks or extensive water rinses. Results show that properties are reasonably degraded by post-treatment washings. X-ray

TABLE VI.
SUMMARY OF TENSILE LAP SHEAR STRENGTHS OF CANDIDATE POLYIMIDE ADHESIVES

ADHESIVE (a)			INITIAL PROPERTIES				POST AGING PROPERTIES (c)			
Panel No.	System	Resin Content % w/w	No. Of Specimens	Shear Strength, psi		Type of Failure	No. Of Specimens	Shear Strength, psi		Type of Failure
				Average Value	Standard Deviation			Average Value	Standard Deviation	
70 & 71	NA/MPD/SDA/BTDA	37.3	5	1664	195	A/P-100	5	884	121	A/P-85
72 & 73	NA/MDA/BTDA	41.5	5	1896	199	A/P-100	5	807	154	A/P-90
74 & 75	NA/MDA/PMDA	50.0	4	1030	191	A/P-100	5	432	173	A/P-100
76 & 77	NA/MPD/BTDA	32.5	5	2178	375	A/P-100	5	1048	124	A/P-80
78 & 79	NA/90MDA: 10SDA/BTDA	35.0	5	2310	255	A/P-100	5	778	87	A/P-80
80 & 81	NA/90MDA: 10SDA/BTDA	38.2	5	1786	270	A/P-100	5	818	42	A/P-75

a) Adhesive process consisted of three coats on 181 glass with A-1100 finish. Titanium 6Al4V was grit blasted followed by a chemical treatment with Pasa-Je! 107. Each panel was first primed with 40% solids BR-34, dried 30 minutes @ 22°F and cured 15 minutes @ 350°F. The first coat then was knife coated with 81% solids BR-34 and dried 30 minutes @ 22°F.

b) A/P - Primer to adhesive failure.

c) Aging cycle was 300 hours at 600°F.

defraction studies of treated metal have not revealed any identifiable fluoride conversion coating. However, by some unexplained mechanism, hydrofluoric acid reacts with the titanium to provide a satisfactory bonding surface.

In another study (Reference 4) involving the bonding of titanium with three different polyimide adhesives, and four pretreatments, it was shown that dry honing with 120 mesh Al_2O_3 grit then rinsing in tap water and followed by a 5 minute immersion in Pasa-Jel 107 (standard grade) for 15 minutes at ambient temperature provided the highest percentage of cohesive failures.

On the basis of these data, it seemed reasonable to assume that Pasa-Jel treatment should be used in the initial screening work. Pretreatment procedure employed was to grit blast (50 micron Al_2O_3) the bond area of the titanium (6Al4V) finger panels followed by tap and distilled water rinses. These panels were immediately immersed in Pasa-Jel 107 (standard grade) for 15 minutes at ambient temperature. The panels were removed, rinsed with tap and distilled water and dried in an air circulating oven at 200°F, with the door opened so that it could be determined when the panels were dry and thus minimize temperature exposure (usually 3 minutes).

This pretreatment method was evaluated using a commercially available polyimide primer and adhesive system (BR-34/FM34) and it was found that the tested panels provided shear strength in the 3000 psi range with good 100% cohesive failure. This observation confirmed the selection of the pretreatment procedure.

3.2 PRIMER COMPOUNDING STUDIES

During the primer compounding studies, four basic approaches to obtaining an adhesive primer that provides good adhesion to titanium alloy at elevated temperatures and which is compatible with TRW "A"-type polyimide were investigated. Details of these evaluations are provided in Appendix C. The approaches studied were:

- Modifications to BR-34 primer
- Evaluation of TRW "A"-type polyimides blended with commercial amide-imide resins
- Evaluation of commercially available high service temperature adhesive primers

- Evaluation of TRW polymers synthesized specifically for this application

The commercially available BR-34 primer was known to provide good adhesion to titanium alloy but during the resin lap-shear screening studies (2.2), it appeared to be incompatible with the TRW "A"-type polyimides. In order to obtain compatibility of the two polymers, several additives to the BR-34 primer were evaluated. These additives included several anhydrides and meta-phenylene diamine. It was concluded from these studies that the proprietary primer BR-34 is made more effective with TRW's "A"-type polymers by the addition of 10 pph nadic anhydride.

A commercially available amide-imide resin, Amoco Chemical Company's polyamide-imide AI-1137, was evaluated as a primer as well as three other proprietary high temperature adhesive primer systems, DuPont PI-4701, Westinghouse B519, and Minnesota Mining and Manufacturing Company's EC-2333. These studies indicated that the amide-imide resin provided good room temperature properties but none of the commercially available compounded primers were suitable for use with "A"-type polyimides.

Evaluation of specially synthesized TRW polymers including long chain polymers and polymers incorporating pendant carboxy and amide groups did not produce satisfactory results.

Finally, evaluation of a blend of Amoco AI-1137 amide-imide resin with one of TRW's polyimide resins provided acceptable properties.

A summary of the data obtained during the primers screening study is provided in Table VII. It is shown that primer combinations of a) BR-34 plus nadic anhydride (Formulation P.3, Table VIII) b) polyamide-imide AI-1137 (Formulation P.1, Table VIII), and c) a 50/50 mixture of polyamide-imide AI-1137 with one of TRW's polyimide resins (Formulation P.2, Table VIII) all provided promising room temperature shear strength data. Further screening at elevated temperature of these primers together with candidate adhesive compounds is discussed in the next section.

3.3 ADHESIVE COMPOUNDING STUDIES

The two candidate adhesive resin systems (NA/MPD/BTDA and NA/90MPD:10SDA/BTDA) were compounded in a similar manner used for the primers to form paste adhesive compounds. These resins in both the compounded and unfilled condition were coated onto glass fabric and scrim to form film adhesives. Details of the above adhesive formulations are provided in Table IX.

An evaluation study of these adhesives in conjunction with the three most promising adhesive primer systems (see Table VIII) was performed again using 6Al-4V titanium lap shear specimens.

The results of this study are shown in Table X. Panel numbers 161 through 164 show the effect of polyamide-imide primer in combination with three candidate compounded adhesive systems. The room temperature shear strength values for all four systems were good, however, the values were low after testing at 600°F. The types of failure obtained indicated the weakness to be the primer system at elevated temperature. Panels number 165 through 167 were prepared to evaluate a primer composed of polyamide-imide and one of TRW's polyimide varnishes. The ambient temperature shear strengths were lower than obtained with AI 1137 but the elevated temperature shear values were higher. This indicated that the addition of TRW polyamic acids improved the thermal stability of the polyamide-imide. Panels 168 through 170 were prepared to evaluate modified BR-34 primer. The ambient temperature values obtained with this primer in conjunction with each of the three candidate adhesive systems were low. The elevated temperature strength retentions were good and the failures were to the glass support. This indicated that a possible weakness of a glass fabric supported system is the silane finish.

To substantiate further the effectiveness of the polyamide-imide resin combined with TRW polyimide resin at elevated temperatures, panel 171 was prepared. An acceptable shear strength of 3740 psi was obtained at room temperature and a strength of 1370 psi was obtained at 600°F after a 10 minute soak.

TABLE VII. SUMMARY OF PRIMERS SCREENING STUDY

PRIMER SYSTEM	LAP SHEAR STRENGTH AT R.T. ⁽¹⁾
Formulation P.3 ⁽²⁾ (Bloomington BR-34 with 10% w/w Nadic Anhydride)	2960
Formulation P.1 ⁽²⁾ (AMOCO AI-1137)	5000
Formulation P.2 ⁽²⁾ (AMOCO AI-1137 with "A"-type Polyimide 50:50)	3620
DuPont PI-5510	1175
Westinghouse B-519	2060
"A"-Type Polyimide with Trimellitic Anhydride Substituted For 50% of Nadic Anhydride	1271

(1) Titanium 6Al4V lap shear specimens bonded with various polyimide adhesives (Reference Tables I through IV). Values reported are the highest obtained from each primer system regardless of the adhesive used.

(2) Reference Table VIII.

TABLE VIII. CONSTITUENTS FOR PRIMER SYSTEMS

Designation	Constituents
P.1	100 p.b.w. AI-1137 100 p.b.w. Aluminum Powder
P.2	50 p.b.w. NA/MPD/BTDA 50 p.b.w. AI-1137 100 p.b.w. Aluminum Powder
P.3	100 p.b.w. BR-34 10 p.b.w. Nadic Anhydride

TABLE IX. CONSTITUENTS FOR ADHESIVE SYSTEMS

Designation	Constituents
A.1.P	50 p.b.w. NA/MPD/BTDA 50 p.b.w. AI-1137 175 p.b.w. Aluminum Powder 5 p.b.w. Cab-O-Sil
A.1.F	Same as above on Style 104 A1100 glass cloth
A.2.F	NA/90MPD:10SDA/BTDA on style 112 A1100 glass cloth
A.3.F	NA/MPD/BTDA on Style 112 A1100 glass cloth
A.4.F	Formulation A.1.P on Style 112 A1100 glass cloth

TABLE X. SUMMARY OF LAP SHEAR DATA FOR ADHESIVE STUDIES

Primer ⁽¹⁾ System	Adhesive ⁽²⁾ System	Panel Number	Room Temperature Environment			600°F Environment		
			Avg. Value	Std. Dev.	Type of Failure	Avg. Value	Std. Dev.	Type of Failure ⁽³⁾
P.1	A.1.P	161	5000	226	C/A 100	214	42	A/P 100
P.1	A.2.F	162	3800	283	A/T 100	211	61	A/P 82
P.1	A.3.F	163	3120	452	A/T 100	99	21	A/P 100
P.1	A.4.F	164	4820	191	A/G 100	72	34	A/P 100
P.2	A.2.F	165	2620	85	A/G 60	734	20	C/A 50
P.2	A.3.F	166	2600	57	C/A 75	854	48	C/P 100
P.2	A.4.F	167	2620	311	A/G 100	566	14	C/P 100
P.3	A.2.F	168	1845	219	C/P 50	986	14	A/G 100
P.3	A.3.F	169	2030	410	A/G 60	1110	42	A/G 100
P.3	A.4.F	170	2440	226	A/G 100	654	72	A/G 100
P.2	A.1.F	171	3740	28	A/P 75	1370	20	C/A 90

(1) See Table VIII for description

(2) See Table IV for description

(3) C/A - Cohesive failure of the adhesive, P/T - Primer to Titanium failure,

A/P - Primer to adhesive failure, A/G - Adhesive to fiberglass support

C/P - Cohesive failure of the primer

These were the best data obtained to date and correlates with previous 600°F exposure obtained during the primer studies (Appendix C). On the basis of the good room and elevated temperature strength data, the adhesive system based on a 50/50 by weight combination of TRW's polymer NA/MPD/BTDA and Amoco polyamide-imide AI-1137 was selected. The TRW polymer varnish containing NA/MPD/BTDA was selected over the one with NA/90MPD:10SDA/BTDA in this combination because this varnish can be prepared readily and presents no stability problems although little difference was obtained in shear strength at both room and elevated temperatures.

Further evaluation of the selected adhesive system (NA/MPD/BTDA and AI-1137) then was performed to determine the most desirable ratio between the two resin systems that provides the best combination of room temperature and 600°F shear strengths. Primers used in these evaluations had the identical ratio of resin constituents as the adhesive formulation. It was shown (Reference Figure 6) that higher proportions of AI-1137 amide-imide resin increased the room temperature shear strength but the data in Figure 7 clearly showed that a 50:50 ratio provided the highest 600°F shear strength data thus substantiating this selection.

3.4 SCREENING TESTS

In order to select the adhesive form (paste or film) for Task III detailed evaluations and to confirm that acceptable properties are provided by the selected primer and adhesive system, a preliminary screening study was performed.

Lap shear (titanium to titanium) and short beam shear (mixture of titanium and boron composite) test specimens, prepared by the procedures described in Appendix D, were tested at room temperature and at 600°F. Properties of the lap shear specimens are reported in Table XI and show comparative values to those obtained during the primer and adhesive compounding studies. The short beam shear test data are reported in Table XII. Ultimate shear strength of the assembly was calculated using the simple formula

$$S_u = \frac{0.75 V}{t b}$$

Where:

- S_u = Nominal shear strength
 V = Load at shear failure
 t = Total specimen thickness
 b = Specimen width

TABLE XI.
 PRELIMINARY SCREENING
 LAP SHEAR STRENGTH DATA
 Titanium to Titanium⁽³⁾

PROPERTY	ADHESIVE TYPE	
	Paste	Film
Strength at R. T., psi	3310	3000
Standard Deviation, psi	164	360
Type of Failure ⁽¹⁾ , % of surface	A/P, 100	C/A, 70
Strength at 600°F, psi ⁽²⁾	1144	1090
Standard Deviation, psi	191	100
Type of Failure ⁽¹⁾ , % of surface area	C/A, 95	C/A, 100
Strength Retention at 600°F, %	35	36

(1) C/A - Cohesive failure of the adhesive
 A/P - Primer to adhesive failure

(2) Conditioned 10 minutes at 600°F before applying load

(3) Fabricated with 0.5-inch overlap and tested at a crosshead speed of .05-inch/minute

Because the short beam shear specimens did not fail catastrophically, the failure was taken to be where the slope of the load line on the stress-strain autograph changed.

Shear stress at the bond line was calculated using the formula

$$\tau = \frac{\frac{V}{bt} \left[\frac{1}{2} \frac{\bar{y}}{t} - \frac{1}{8} \right]}{\left[\left(\frac{1}{24} \right) - \left(\frac{1}{4} \right) \left(\frac{\bar{y}}{t} \right) + \left(\frac{\bar{y}}{t} \right)^2 \left(\frac{1}{2} \right) + \frac{E_B}{E_A} \left\{ \left(\frac{1}{3} \right) - \left(\frac{\bar{y}}{t} \right) + \left(\frac{\bar{y}}{t} \right)^2 - \left(\frac{1}{24} \right) + \left(\frac{1}{4} \right) \left(\frac{\bar{y}}{t} \right) - \left(\frac{\bar{y}}{t} \right)^2 \left(\frac{1}{2} \right) \right\} \right]}$$

When:

$$\bar{y} = \left(\frac{t}{2}\right) \left[\left(\frac{1}{4}\right) + \frac{E_B}{E_A} \cdot \left(\frac{3}{4}\right) \right] / \left[\left(\frac{1}{2}\right) + \left(\frac{1}{2}\right) \frac{E_B}{E_A} \right]$$

Where:

t = Total Specimen Thickness

b = Specimen Width

V = Shear Force = $\frac{\text{Ultimate Load}}{2}$

E_A = Modulus of Material A (Tension face)

E_B = Modulus of Material B (Compression face)

τ = Shear Stress at Bond Line

The data presented in Tables XI and XII indicated that there was no significant difference between the adhesive properties of paste and film forms of TRW "A"-type polyimide adhesives. However, because the mode of failure in the lap shear specimens using the film form was cohesive at both room temperature and 600°F, the glass scrim carrier was suspected of propagating bond rupture. This suspicion was based upon the fact that examination of cohesive failures with the film adhesive showed exposed glass fibers thus indicating an adhesive failure to the glass. (Because the surface area of the exposed glass was very small, the predominant failure therefore was interpreted to be cohesive). From this observation it was assumed that assemblies bonded with paste adhesive would probably provide better reliability under long term stress applications. Also, the paste adhesive was easier to apply since it was imidized after application to the faying surfaces and thus adhered to the surface during pre-cure assembly.

For the preceding reasons, the system selected for Task III detailed evaluation studies was the AIP paste adhesive containing 50/50 parts by weight combination of TRW's polymer NA/MPD/BTDA and Amoco polymer AI-1137 plus 175 parts by weight aluminum powder and 5 parts by weight Cab-O-Sil. Primer system P.2 containing the same polymer combination as the adhesive but with only 100 parts by weight aluminum powder, was selected for priming all faying surfaces.

TABLE XII. PRELIMINARY SCREENING SHORT BEAM SHEAR DATA

ADHERENDS		ADHESIVE FORM	ROOM TEMPERATURE TESTS				600°F TESTS (4)		STRESS (2) At Bondline psi	STRENGTH RETENTION AT 600°F % (3)
Material A	Material B		NOMINAL STRENGTH		Stress (1) At Bondline psi	NOMINAL STRENGTH				
			Average Value	Standard Deviation		Average Value	Standard Deviation			
Titanium	Titanium	Film	19,550	630	19,110	8860	560	8810	46	
Titanium	Titanium	Paste	20,140	1830	19,730	9340	410	9190	46	
Boron Composite	Titanium	Film	11,220	540	10,940	7120	690	7090	63	
Boron Composite	Titanium	Paste	10,450	630	10,170	7120	560	7080	68	
Boron-PI Prepreg (Primary) (Bond)	Titanium	Primer Only	12,910	1400	12,610	6720	560	6610	52	

(1) - Titanium 6A14V Alloy Modulus 15×10^6 psi; Boron Composite Modulus 27×10^6 psi.(2) - Titanium 6A14V Alloy Modulus 13.5×10^6 psi; Boron Composite Modulus 20×10^6 psi.(3) - Ultimate Stress at 600°F $\times 100$
Ultimate Stress at R.T.

(4) - Conditioned 10 minutes at 600°F before applying load.

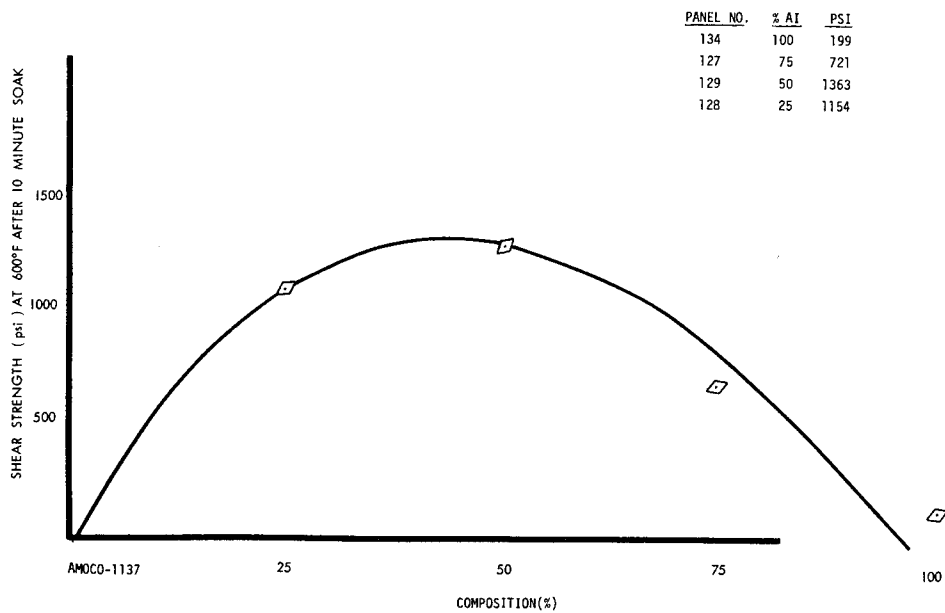
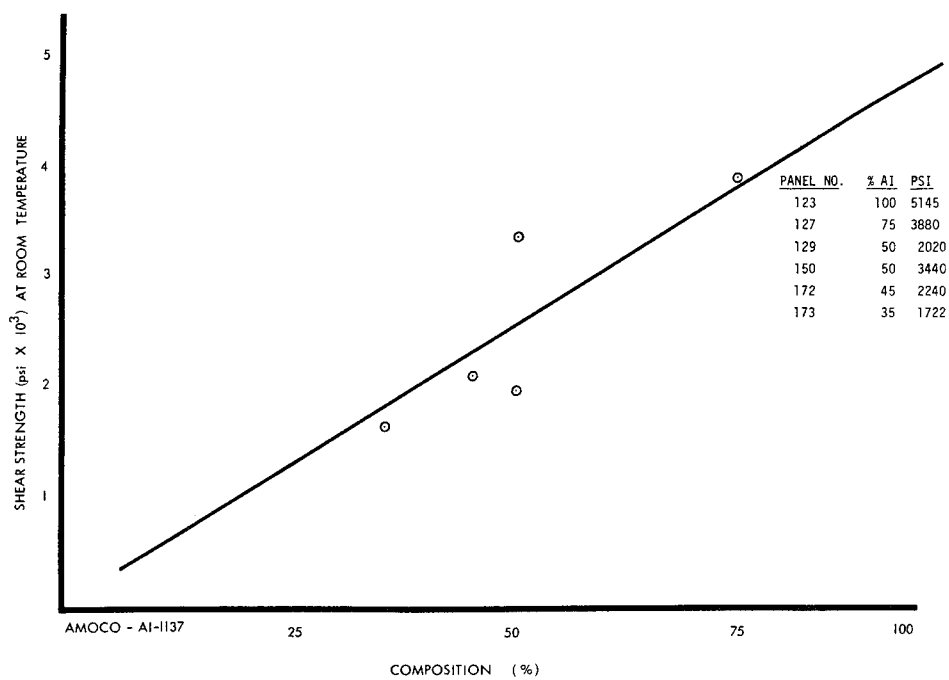


Figure 7. Effect Of Amide-Imide (AMOCO-1137) Composition On Lap Shear Strength At 600°F

4. TASK III - DETAILED EVALUATION OF SELECTED POLYIMIDE ADHESIVE SYSTEM

Lap shear and short beam shear specimens were prepared by the procedures described in Appendix D using Primer P.2 and Adhesive A.1.P. These were prepared in sufficient quantities to provide NASA Langley Research Center with one hundred lap shear specimens and four hundred of each configuration short beam shear specimens as well as for the detailed evaluations performed by TRW Systems. Discussion of the evaluations performed by TRW Systems is provided in the following section.

4.1 QUALITY CONTROL TESTS

A random selection was made from the short beam shear test specimens which then were tested at room temperature in accordance with the procedures defined in 3.4. Properties of these specimens are presented in Table XIII. It is seen from these data that the variance between the average quality control test results and the corresponding average preliminary screening test results (Table XII) are:

- -16% for titanium to titanium bonds
- +7% for titanium to boron composite secondary bonds
- -10% for titanium to boron composite primary bonds.

4.2 LOW TEMPERATURE TESTS

Short beam shear test specimens of the three configurations were tested at -65°F after conditioning them in the test chamber at -65°F for 10 minutes prior to loading. The load was applied through a single point at a loading rate of 0.05-inch/min, the span to depth ratio for these specimens was 4:1. Properties of these specimens are provided in Table XIV.

4.3 ELEVATED TEMPERATURE TESTS

Specimens were tested at 600°F in the same manner as described in 3.4. Properties of these specimens are presented in Table XV. The variance between the average properties of these specimens and the corresponding average preliminary screening test results (Table XII) are:

- +12% for titanium to titanium bonds
- +10% for titanium to boron composite secondary bonds
- +29% for titanium to boron composite primary bonds.

TABLE XIII. QUALITY CONTROL TESTS⁽¹⁾

ADHERENDS		NOMINAL STRENGTH, psi		AVERAGE ⁽²⁾ STRESS AT BONDLINE psi
Material A	Material B	AVERAGE VALUE psi	STANDARD DEVIATION	
Titanium	Titanium	16882	212	16880
Boron Composite	Titanium	11212	233	11720
Boron-PI Prepreg (Primary Bond)	Titanium	11600	413	11070

(1) Short beam shear tests at room temperature, 4:1 span to depth ratio, 25 specimens.

(2) Titanium alloy 6Al-4V E = 15 Msi, Boron composite E = 27 Msi

TABLE XIV. SHORT BEAM SHEAR TESTS AT -65°F

ADHERENDS		NOMINAL STRENGTH, psi		STRENGTH ⁽¹⁾ RETENTION %
Material A	Material B	NOMINAL STRENGTH	STANDARD DEVIATION psi	
Titanium	Titanium	24720	1079	146
Boron Composite	Titanium	16460	451	146
Boron-PI Prepreg (Primary bond)	Titanium	14040	345	120

(1) $\frac{\text{Strength At } -65^{\circ}\text{F}}{\text{Strength At R.T.}} \times 100$
(Per Table I)

(2) Quintruplicate samples

TABLE XV. SHORT BEAM SHEAR TESTS AT 600°F

ADHERENDS		NOMINAL STRENGTH, psi		STRENGTH RETENTION % ⁽¹⁾	AVERAGE ⁽²⁾ STRESS AT BONDLINE psi
Material A	Material B	AVERAGE STRENGTH	STANDARD DEVIATION psi		
Titanium	Titanium	10400	403	62	10265
Boron Composite	Titanium	7780	120	70	7829
Boron-PI Prepreg (Primary bond)	Titanium	8500	170	73	8473

(1) $\frac{\text{Strength At } 600^{\circ}\text{F}}{\text{Strength at R.T.}} \times 100$
(Per Table I)

(2) Titanium alloy 6Al4V E = 13.5 Msi
Boron Composite E = 20.0 Msi

(3) Quintuplicate samples

4.4 AGING TESTS

Short beam shear test specimens were aged at -65°F and at 600°F in air. The -65°F aging was performed in a Conrad-Missimer test chamber cooled with refrigerated circulating air. Elevated temperature aging at 600°F was conducted in an air circulating oven with a horizontal air velocity of 250 feet/min and an air change rate of 400 cubic feet/min. Bond lines were parallel to the air flow. Specimens were withdrawn after 500 and 1000 hour intervals and weight-loss and resin content percentages were determined on these specimens using the following calculations:

$$L_s = \frac{100 \cdot W_{s_1} - W_{s_2}}{W_{s_1}}$$

$$L_r = \frac{100 \cdot L_s}{R_c}$$

When:

$$R_c = \frac{100 \cdot W_{s_1} - W_b - W_g - W_t}{W_{s_1}}$$

Where:

W_{s_1} = Weight of unaged specimen

W_{s_2} = Weight of aged specimen

W_b = Weight of boron filament

W_g = Weight of glass scrim cloth

W_t = Weight of titanium alloy sheet

L_s = Actual weight loss of specimen, %

L_r = Resin weight loss, %

R_c = Resin content, % wt.

Flexural properties then were determined at room temperature and the resultant data are provided in Table XVI for the 600°F aging, and in Table XVII for the -65°F aging.

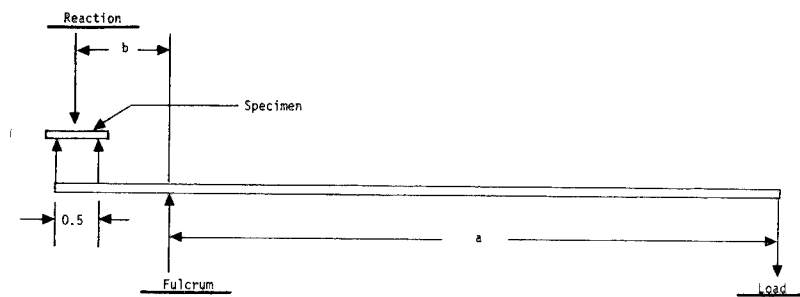
After 1000 hours aging at 600°F, both the primary and secondary bonded titanium/boron composites lost approximately 30% of their resin content and were delaminated upon removal from the aging oven. (This weight loss is attributed to loss of the composite's resin matrix rather than the adhesive resin).

Shear strength retention at room temperature after aging at 600°F was generally good. The all titanium specimens showed a slight initial increase in strength, and maintained their strength after 1000 hours of aging. Primary bonded composite specimens showed a slightly lower strength retention after 500 hours of aging than did the secondary bonded specimens, but both types of specimens failed after 1000 hours aging. Specimens aged at -65°F showed a small increase in weight up to 500 hours, and then showed a weight decrease at 1000 hours aging.

Shear strength data shows that the -65°F aging had negligible effects upon the room temperature strengths of all titanium specimens. Primary bonded composite specimens had slightly lower strength retention than the secondary bonded composite specimens after aging for any given period at -65°F.

4.5 STRESS RUPTURE TESTS

Primary bonded short beam specimens were tested at 600°F in triplicate at stress levels of 94%, 75%, 50%, 25% and 20% of the average shear strength at 600°F reported in Table XV. The short beam shear specimens were installed individually in three stress rupture jigs (Figure 8 and 9) located inside the test chamber. Load was applied to the specimens by means of a dead weight applied to the test jig's lever arm. Temperature in the test chamber

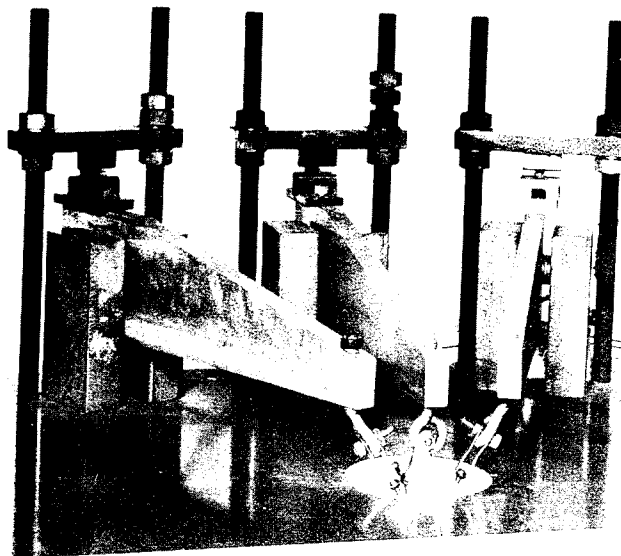


Lever Arm Ratios (1)

Jig	a : b Ratio
1	6'8 : 1
2	6'5 : 1
3	6'9 : 1

(1) Test jigs were calibrated using load cells at the reaction point and dead weight loads.

Figure 8. Schematic of Test Fixtures



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Figure 9. Stress Rupture Test Jig

TABLE XVI. SHORT BEAM SHEAR PROPERTIES OF SPECIMENS AGED AT 600°F

Type of Specimen	Hours of Aging at 600°F	Actual Weight ⁽²⁾ Loss %	Calculated ⁽¹⁾ Resin Weight Loss %	NOMINAL SHEAR STRENGTH, psi		
				Average Value	Standard Deviation	Retention %
Titanium to Titanium	100	0.185	Not Applicable	19.12	0.59	111
	500	0.421		16.00	1.02	94
	1000	0.533		17.97	0.67	103
Titanium to Boron Composite Primary Bond	100	0.805	3.84	11.45	0.42	99
	500	2.47	11.7	9.70	0.29	83
	1000	6.237	29.6	(3)	(3)	(3)
Titanium to Boron Composite Secondary Bond	100	1.146	5.48	10.51	1.28	93
	500	2.24	10.7	10.39	1.07	92
	1000	6.397	30.2	(3)	(3)	(3)

(1) Based upon a specimen original resin content of 21% weight.

(2) Average of five specimens tested at room temperature using a single point flexural loading at 4:1 span to depth ratio.

(3) Delaminated during aging.

TABLE XVII. SHORT BEAM SHEAR PROPERTIES OF SPECIMENS AGED AT -65°F

Type of Specimen	Hours of Aging at -65°F	Weight Change ⁽¹⁾ %	NOMINAL SHEAR STRENGTH, psi		
			Average Value	Std. Deviation	Retention %
Titanium to Titanium	100	+0.321	14.55	2.30	86
	500	+0.457	17.96	1.35	103
	1000	-0.096	17.39	1.62	101
Titanium to Boron Composite Primary Bond	100	+0.522	9.33	0.40	81
	1000	+0.319	9.38	1.01	81
Titanium to Boron Composite Secondary Bond	100	+0.485	10.17	0.90	91
	500	+0.503	9.59	0.10	85
	1000	+0.118	9.65	0.15	86

(1) Average of five specimens tested at room temperature using a single point flexural loading at 4:1 span to depth ratio.

was maintained at 600°F by circulating air. Time to rupture was monitored by measuring the specimens deflection while under load both by visual measurement and autographically recording the time at which the specimens' previously determined deflection-at-failure at 600°F was exceeded. Weight-loss was determined on the failed specimens after removal from the test jig, and the average weight-loss percentage is presented in Table XVIII. It was observed that, in the case of the 50%, 25% and 20% stress level tests, surface filaments and resin were inadvertently lost while removing the specimens from the test jig. Therefore, the value shown in Table XVIII not only represents weight-loss by thermo-oxidative degradation, but also includes additional weight-loss as a result of handling. Figure 10 provides a graphical presentation of the time to rupture at 600°F for specimens under various stress levels. Specimens loaded at 20% stress level did not produce a failure after 1000 hours of test.

5. STRUCTURAL ANALYSIS

This section presents the formulas employed to calculate stresses in short beam shear specimens composed of two materials, comments on the validity of such test data for design, and comments on the delamination of boron laminate-titanium specimens during long term exposure at elevated temperature in both stressed and unstressed conditions.

5.1 ANALYSIS OF TWO MATERIAL SHORT-BEAM SPECIMEN

The specimen geometry and shear and moment diagrams are shown in Figure 11. The usual assumptions of a strength of materials treatment of flexure yield the following relationships:

5.1.1 Shear Stress At Any Depth In A Two Material Short Beam Specimen

Within Material 1

$$0 \leq y \leq t_1$$

$$\tau_1 = (3V/2Wt) [2y\bar{y}/t^2 - y^2/t^2] /$$

$$[(E_2/E_1) (1 - 3\bar{y}/t + 3\bar{y}^2/t^2)$$

$$+ (1 - E_2/E_1) (t_1^3/t^3 - 3t_1^2\bar{y}/t^3 + 3t_1\bar{y}^2/t^3)]$$

TABLE XVIII.
STRESS RUPTURE AND WEIGHT LOSS
TESTS AT 600°F

Stress Level %	Stress ⁽⁴⁾ Loading Ksi	HOURS TO FAILURE		Actual ⁽¹⁾ Weight-Loss %	Calculated ⁽²⁾ Resin Weight Loss %
		Time	Std. Deviation		
94	7.99	10	0.5	0	0
75	6.38	94	3.5	0.838	4.000
50	4.25	267	1.0	4.42 ⁽³⁾	21.0
25	2.22	750	3.0	7.65 ⁽³⁾	36.2 ⁽³⁾
20	1.78	>1000 ⁽⁴⁾	--	7.53 ⁽³⁾	36.5 ⁽³⁾

- (1) Average of (3) specimens.
 (2) Based upon a specimen original resin content of 21 percent weight.
 (3) Undetermined quantity of resin and/or filaments were lost while removing from test jig. Therefore, this value does not totally represent thermo-oxidative degradation.
 (4) No failure occurred up to 1000 hours loading at 20% stress level.

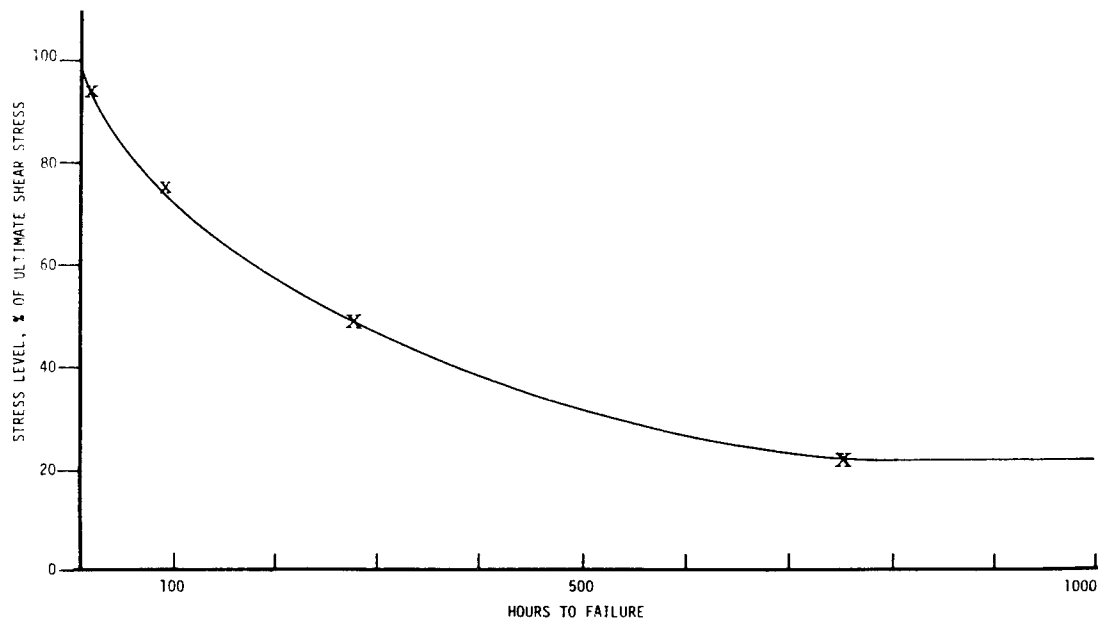


Figure 10. Stress Rupture Tests at 600°F

Within Material 2

$$t_1 \leq y \leq t$$

$$\tau_2 = (3V/2Wt) [1 - 2 \bar{y}/t + 2 y\bar{y}/t^2 - y^2/t^2] /$$

$$[(1-3\bar{y}/t + 3 \bar{y}^2/t^2)$$

$$+(E_1/E_2 - 1) (t_1^3/t^3 - 3t_1^2 \bar{y}/t^3 + 3t_1 \bar{y}^2/t^3)]$$

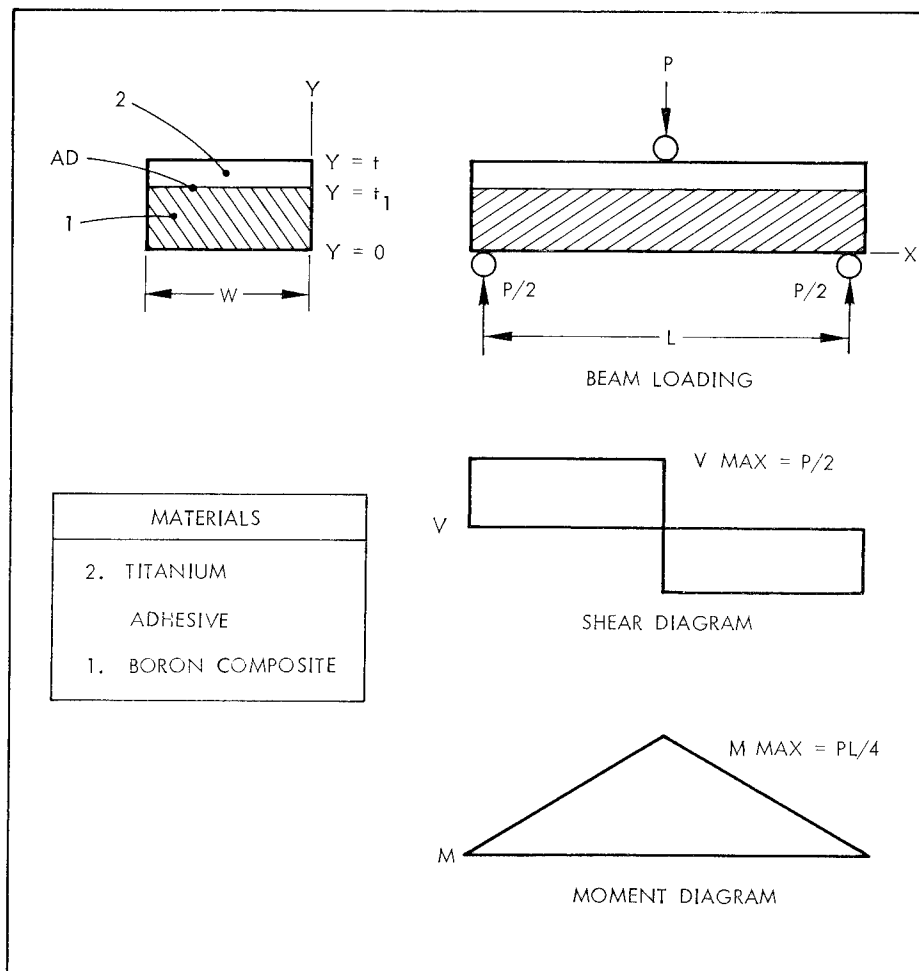


Figure 11. Geometry of Two Material Short Beam Shear Specimen For Evaluation of Adhesive Bond Strengths

When:
$$\bar{y} = (t/2) [1 + (E_1/E_2 - 1) t_1^2/t^2] / [1 + (E_1/E_2 - 1) t_1 / t]$$

Where: τ_1 = Shear stress in material 1
 τ_2 = Shear stress in material 2
 \bar{y} = Location of neutral axis
 t = Total thickness
 t_1 = Thickness of material No. 1 on tension side
 E_1 = Modulus of elasticity in flexure of material No. 1 on tension side
 E_2 = Modulus of elasticity in flexure of material No. 2 on compression side
 V = Shear Force = 1/2 applied load P
 W = Specimen width
 y = Distance from bottom face to lamina on which calculated shear stress acts

5.1.2 Flexure Stress At Any Depth In A Two-Material Short Beam Specimen

Within Material No. 1 (bottom side, tension)

$$\sigma_1 = (3PL/4Wt^3) (\bar{y} - y) / [(E_2/E_1) (1 - 3\bar{y}/t + 3\bar{y}^2/t^2) + (1 - E_2/E_1) (t_1^3/t^3 - 3t_1^2 \bar{y}/t^3 + 3t_1 \bar{y}^2/t^3)]$$

Within Material No. 2 (top side, compression)

$$\sigma_2 = (3PL / 4Wt^3) (E_2/E_1) (y-\bar{y}) / [(E_2/E_1) (1 - 3\bar{y}/t + 3\bar{y}^2/t^2) + (1 - E_1/E_2) (t_1^3 / t^3 - 3t_1^2 \bar{y}/t^3 + 3t_1 \bar{y}^2/t^3)]$$

Where L = Length of specimen between horizontal supports

σ_1 = Flexural Stress In Material 1

σ_2 = Flexural Stress In Material 2

5.1.3 Shear Stress At The Bond Line In A Short Beam Specimen With Two Components Of Equal Thickness ($t_1 = t/2 : y = t/2$)

$$\tau_{\text{bond line}} = (3V/2Wt) \left[\bar{y}/t - 1/4 \right] /$$

$$\left[(E_2 / E_1) (1 - 3 \bar{y}/t + 3 \bar{y}^2/t^2) \right.$$

$$\left. + (1 - E_2/E_1) (1/8 - 3\bar{y}/4t + 3\bar{y}^2/2t^2) \right]$$

Where

$$\bar{y} = (t/2) [1/2 + 1 / (1 + E_1/E_2)]$$

5.1.4 Maximum Shear Stress Within Material No. 1 In A Short Beam Specimen With Two Components Of Equal Thickness

$$\tau_{1 \text{ max}} = \tau_{\text{bondline}} \left[(3+E_1/E_2)^2 / 8 (1+E_1/E_2) \right]$$

5.1.5 Maximum Compressive Stress In Top Fiber Of Material No. 2 In A Short Beam Specimen With Two Components Of Equal Thickness

$$\sigma_{2 \text{ max}} = \tau_{\text{bondline}} \left[(3+E_1/E_2)(L/2t) \right]$$

5.1.6 Maximum Tensile Stress In bottom Fiber Of Material No. 1 In A Short Beam Specimen With Two Components Of Equal Thickness

$$\sigma_{1 \text{ max}} = \tau_{\text{bondline}} \left[(E_1/E_2) (3+E_1/E_2) (L/2t) \right]$$

5.2 APPLICATIONS OF THE ANALYSIS

The specimen employed in the program was composed of equal thicknesses of boron laminate and titanium or two pieces of titanium. Dimensions were:

$$\begin{array}{ll} t = 0.125 & W = 0.260 \\ t_1 = 0.0625 & L = 0.50 \end{array}$$

The materials were tested at room temperature and 600°F; the elastic moduli were:

	R. T.	600°F
$E_1 = (\text{Boron}) \text{ psi}$	27×10^6	20×10^6
$E_2 = (\text{Ti-6Al-4V}) \text{ psi}$	15×10^6	13.5×10^6
E_1/E_2	1.80	1.48

One question which arose was the possibility of yielding the upper material, titanium, before shear failure. From MIL-HDBK-5, 5.4.6.1, annealed Ti-6Al-4V yields in compression (F_{cy}) at 138 and 92 ksi at R.T. and 600°F respectively. Substituting these values, and the dimensions in 5.1.3 and 5.1.5 it is found that 0.2 percent offset yield is reached when the calculated bondline stress is 19.3 and 12.5 ksi at room temperature and 600°F. These values are greater than any experimental results, so yielding of the titanium was not a problem with the two material specimens. However, for a titanium-titanium bonded specimen the relation (Reference 5.1.5) reduces to $\tau = F_{cy}/8$ when yielding occurs; τ bondline = 17.2 and 11.5 ksi at room temperature and 600°F respectively. Calculated bondline stresses for some titanium-titanium specimens exceeded these yield values. Such values should be corrected down to the calculated bondline stress when yield was reached.

Because the maximum shear stress does not occur at the bondline but rather within the stiffer member of a two material specimen with components of equal thickness, the actual maximum shear stress must be known. From the equation in 5.1.4 and the properties given the maximum shear stress in the boron is within 3 percent and 1 percent of the calculated bondline stress at room temperature and 600°F respectively.

The constancy of applied stress on the bondline of a two-material specimen during creep rupture testing at 600°F was addressed as follows. As a reasonable assumption, titanium will not lose modulus appreciably at this temperature. The bondline stress will change however, if the modulus of the boron laminate changes. If the laminate modulus decreases 10 percent, from 13.5 to 12.15×10^6 psi, the shear stress at the bondline from the equation in 5.1.4 increases by almost exactly 10 percent. It was concluded that this variation was acceptable for the purposes of the test.

5.3 APPLICABILITY OF SHORT BEAM SHEAR DATA AND LAP SHEAR DATA FOR DESIGN

A single lap shear test, as is well-known, produces large tensile stresses at the ends of the lap because of elastic bending of the substrates. These tensile stresses are superimposed on the inherent peaking of shear stresses at the ends in any bonded joint, and shrinkage stresses arising during fabrication and environmental exposure. The susceptibility of an adhesive to fracture from peel loading will be emphasized by the single lap shear test, the lower failure properties being obtained with longer over-lap. In general, a soft, weak, ductile adhesive will seem superior to a strong, stiff adhesive with limited ductility when subjected to this test. Such data are appropriate for structural configurations in which short lengths of boron composite are bonded in regions of the beam where high loads and moments are carried, i.e., as reinforcing splices.

On the other hand, the single lap shear data are far too conservative for structures in which long strips of boron composite are employed, such that the ends are bonded in areas where deformations are low. The boron in this case would be added largely for its stiffness to prevent crippling of the compression flange of a beam and to limit deflections. A short beam shear test would provide a more meaningful indication of adhesive behavior in this situation, because the tendency to peel is not present. Short beam shear test data are unconservative to some degree because compressive stresses over part of the bondline will reduce the tendency to flow or fracture at any given shear stresses. Therefore, it is concluded that lap shear data and short beam data represent lower and upper bounds respectively, on the usable bond strength. An illustration of this is seen in that room temperature short beam shear strength of boron-titanium specimens was equal to the strength of an all-boron specimen of the same thickness. In this case the upper bound was obviously reached.

5.4 DELAMINATION OF UNLOADED TWO-MATERIAL BONDED SPECIMENS AT 600°F

Some boron laminate-titanium two material specimens delaminated after extended exposure at 600°F, unloaded. The separation apparently occurred in the boron laminate adjacent to the bondline. Assuming that the delamination was caused by mechanical as well as chemical effects, it seems reasonable to speculate as follows. The bondline as fabricated is stress free at 600°F,

the cure temperature. At lower temperature, e.g. room temperature, the bondline is stressed by differential thermal contraction of the two materials, and the specimen exhibits a natural curvature. Stresses which developed on extended exposure to 600°F, resulting in delamination, presumably resulted from dimensional change of the boron laminate. Laminate strength also degraded probably until finally the developed stresses exceeded the available strength. Therefore, it is assumed that the flexibility of the titanium may have permitted some reduction of the stresses by bowing. In another configuration with a thin layer of boron bonded to a thick piece of titanium, delamination might occur at shorter times or lower temperatures.

6. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this developmental effort to formulate and characterize new thermally stable adhesives. Based on these findings, recommendations are given for further material and process improvement studies.

6.1 CONCLUSIONS

1. A new adhesive compound consisting of TRW "A"-type polyimide blended with Amoco AI-1137 amide-imide resin, aluminum powder, thixotropic agent (Cab-O-Sil) and solvent (dimethylformamide) was identified as providing shear strengths in titanium-titanium and titanium-boron composite bonded joints above strengths obtained from the state-of-the-art adhesives.
2. The new adhesive compound developed during this study was identified as possessing excellent thermo-oxidative stability and strength retention after long term exposure at 600°F in either stressed or unstressed conditions.

3. A specific TRW "A"-type polyimide composition was identified as being most suitable for use in adhesive compounds. This composition consisted of nadic anhydride, meta-phenylene diamine, and benzophenone tetracarboxylic acid dianhydride combined in dimethylformamide to yield a 1100 formulated molecular weight.
4. Structural analysis of the short beam shear strength data showed that the limiting factor in the case of adhesively bonded titanium-boron composite assemblies was the boron composite's shear strength.
5. Variations in the ratio between TRW "A"-type polyimide and AI-1137 amide-imide in the adhesive compound were shown to either increase the resultant bonded assemblies shear strength at room temperature and decrease the strength retention at 600°F or vice-versa for the corresponding opposite ratio variance.
6. Balanced assemblies, i.e. assemblies consisting of one substrate sandwiched between two elements of the other were shown to be practical for structural applications. Bonded assemblies consisting of one layer each titanium alloy and boron composite demonstrated severe bowing caused by large differences in the coefficient of thermal expansion between the two materials. This did not significantly affect the assemblies shear strength thus confirming the balanced assemblies approach.
7. Processing was developed for the fabrication of bonded assemblies in heated presses. The moderate bonding pressure (150 psig) with a 600°F curing temperature for a short curing time (sixty minutes) used in these studies demonstrated industrially acceptable bonding cycles.

6.2 RECOMMENDATIONS

1. Further study of glue-line thickness variations and the effects of processing on glue-line thickness is warranted in order to optimize adhesive properties and to establish a reproducibility factor.
2. Study of the adhesive compounds shelf life stability is warranted in order to establish manufacturing limits for scaled-up applications of this compound.
3. Evaluation of this adhesive compound with other substrates, e.g. stainless steel, graphite-composites, and other titanium alloys, is necessary. Additional constituents such as oxidation scavengers for the stainless steel alloys may be required.
4. Evaluation of this adhesive and development of processes for bonding honeycomb sandwich assemblies is warranted in order to extend the scope of applicability for this system.
5. Modification to this adhesive and development of autoclave bonding processes is recommended in order to define its potential for this application.
6. Development of new polymers that will combine the adhesive features of the amide-imide polymer and the thermal stability of the "A"-type polyimide polymers is necessary in order to increase the 600°F strength retention above the 73% obtained during this program.

7. NEW TECHNOLOGY

This section provides discussions of the new adhesive technology developed during this program.

7.1 STRUCTURAL ADHESIVE FOR HIGH TEMPERATURE APPLICATIONS

Adhesive compound formulations were developed consisting of TRW "A"-type polyimide resin, an amide-imide resin (AI-1137), aluminum powder,

thixotropic agent (Cab-O-Sil) and solvent (dimethylformamide). A specific "A"-type polyimide resin composition was identified as being the most suitable of the resin formulations evaluated for application in adhesive compounds. This composition consisted of nadic anhydride, meta-phenylene diamine and benzophenone tetracarboxylic acid dianhydride. These specific combinations of constituents and copolymeric blends provided a good balance between the excellent thermal stability of the "A"-type polyimide resins and the excellent room temperature adhesive properties of the amide-imide resin.

APPENDIX A

DETAILS OF POLYMER AND PREPOLYMER SYNTHESIS

A-1 VARNISH SYNTHESIS

The following amic-acid (A-A) synthesis method was used for the preparation of all six varnish formulations:

A quantity of diamine was dissolved in DMF and cooled to 20°C with an ice bath. To this solution was added NA in DMF, during which time the temperature was maintained at 30°C by means of an ice bath. This mixture was treated with the addition of a slurry consisting of dianhydride in DMF. The resulting 40% solids loaded solution was stirred at ambient temperature for one hour.

A-2 PREPARATION OF POLYIMIDE PREPOLYMER MOLDING POWDERS

The varnishes were placed on a rotary evaporator and approximately 90% of the DMF was removed under vacuum at 300°F. The tacky powders were isolated, then dried (imidized) at 250-300°F in a forced air oven for two to four hours. Each prepolymer was checked for conversion to the desired imide linkage by infrared analysis.

APPENDIX B.

LAP SHEAR SPECIMEN PREPARATION STUDIES

Initial studies for preparing lap shear specimens were performed with unsupported "A"-type polyimide resins. The following discussions present data for representative test panels; data which are not reported (missing panel numbers) were for panels which represented process duplications not worthy of discussion. Panels number 1 and 2 were first attempts to obtain familiarization of processing characteristics and strength levels for "A"-type polyimide systems as adhesives (Reference Table BI). These panels were primed with Bloomingdale BR-34 polyimide adhesive primer reduced to 27% w/w solids from 81% w/w with dimethyl formamide (DMF) and dried 30 minutes at 220°F. Panels number 3 and 4 were not primed but bonded in the same manner as 1 and 2 to determine primer effectiveness. The results (Table BI) indicate the need to prime the titanium surface. The necessity for a primer with P13N adhesive also was substantiated when P13N was used as a supported film (Reference Panel 53 of Table BII) without a primer which failed adhesively to the titanium at only a slightly higher level than the unsupported panels 3 and 4.

The reasons for the inconsistent results on panels 1 to 4 (Table BI) are believed to be a result of poor pressure control and the use of a 0.010-inch spacer in the bond fixture. The measured bondlines of the cured specimens were from .007 to .008-inch thick, yet the tested bond area was starved and cellular (foamed) in structure.

In order to correct the cellular (foamed) structure of the resin and to reduce the starved appearance of the bondline, the P13N resin was filled with milled glass fibers. The shear strength of lap shear specimens was increased slightly as shown in panel 7 of Table BI, the resultant bondlines were .008 to .012-inch thick, but with a cellular looking resin structure.

In parallel studies, panel 11 of Table BI was prepared to confirm the effectiveness of the pretreatment procedure. The dimethyl formamide diluted BR-34 primer was brush applied and cured at 550°F followed by application of the unaltered 81% w/w solids primer (as supplied by the vendor) which was used as the adhesive on this panel. The strengths were slightly lower than Bloomingdale Rubber Company reports when using a style 112 glass fabric

TABLE BI. SUMMARY OF TYPICAL UNSUPPORTED TITANIUM (6A1-4V) TENSILE LAP SHEAR STRENGTH DATA

Panel No.	PRIMER			ADHESIVE						TENSILE LAP SHEAR STRENGTH			
	System	Solids % w.w	Processed	System	Solids % w.w	Processed	Curing			No. of Test Specimens	R. T. psi	Standard Deviation psi	Type Failure % Surface Area
							Pressure psig	Temp. °F	Time Min.				
1 & 2	BR-34	27	30 min. @ 220°F	P13N	40	15 min. @ 300°F	200	350	30	10	1070	296	P/T-80
3 & 4	None	--	--	P13N	40	15 min. @ 300°F	200	550	30	10	540	114	--
7	BR-34	27	15 min. @ 220°F	P13N 30pph milled glass fibers	40 (Resin)	4 min. @ 375°F 4 min. @ 475°F	200	600	30	5	747	47	C/A-85
11	BR-34	27	30 min. @ 220°F 30 min. @ 550°F	BR-34	81	30 min. @ 220°F	200	550	30	5	2470	178	C/A-100
15	BR-34	27	30 min. @ 220°F	P13N	40	4 min. @ 225°F 4 min. @ 375°F	200	550	30	5	577	148	A/P-70
16	BR-34	27	30 min. @ 220°F 15 min. @ 550°F	P13N	40	30 min. @ 220°F	200	550	30	5	883	59	C/A-100
18	BR-34	81	5 min. @ 225°F 5 min. @ 550°F	P13N	40	5 min. @ 225°F	200	550	30	5	1224	323	C/A-100
22	BR-34	27	30 min. @ 220°F 15 min. @ 550°F	P13N 167pph -325 mesh Titanium	40 (Resin)	10 min. @ 220°F	200	550	30	5	982	146	C/A-100
24	BR-34	81	30 min. @ 220°F 15 min. @ 550°F	P13N 167pph -325 mesh Titanium	40 (Resin)	10 min. @ 225°F	200	550	30	5	1241	70	---
25	BR-34	81	30 min. @ 220°F	P13N	40	15 min. @ 220°F	200	550	30	5	1952	632	A/P-60
26	BR-34	81	30 min. @ 220°F 15 min. @ 550°F	P13N	40	30 min. @ 220°F	200	550	30	5	1026	242	C/A-100

C/A - Cohesive failure of the adhesive
P/T - Primer to Titanium failure

A/P - Primer to Adhesive Failure

supported FM-34 adhesive film. A cohesive failure occurred confirming that the combination of the pretreatment with the diluted primer are compatible.

In an effort to reduce the cellular structure of the bondline, panel 15 was bonded with P13N resin preimidized on the specimen. The resulting low shear strength level (Table BI) was attributed to not exposing the primer to the cure temperature prior to over-coating with P13N thus obscuring the cellularity of the bondline. Panel 16 (Table BI) showed no improvement when the diluted primer was cured first at 550°F and then over-coated with P13N adhesive. The low shear strength of this panel again is accounted for by the cellular structure of the bondline. Panel 18 was primed with the 81% w/w solids BR-34 to obtain a more complete coverage of the metal and P13N adhesive was utilized. The improvement in shear strength over that of panel 16 (Table BI) indicated that dilution of the primer is not as effective as the 81% w/w solids material when used with P13N resin. Panel 18 still had a cellular bondline indicating less than optimum strength had been achieved. Panels 22 and 24 were primed at two levels of primer solids and bonded with P13N filled with titanium metal (-325 mesh). Once again the specimens prepared with the 81% w/w solids primer (panel 24) showed some advantage over the diluted primer. The effect of adding titanium metal powder offered no strength advantage as shown by comparing panels 24 and 18 (1241 vs. 1224 psi respectively). Panels 25 and 26 were prepared to determine the effect of co-curing the 81% solids primer with P13N adhesive. Higher shear values were obtained with the co-cured primer, but it was observed that a blend of primer and adhesive resulted. The shear strength obtained in these experiments was a measure of the strength of the primer and adhesive mixture rather than of the P13N itself. Various degrees of mixing accounted for the large standard deviation. Panel 26 (Table BI) had lower strength than panel 25 which was attributed to the fine foam structure of the bondline.

Although it was not originally proposed to perform supported adhesive studies at this time, some work was initiated to determine whether higher shear values could be obtained and thus ensure a better shear strength screening technique for the six candidate adhesives. Some of these are reported in Table BII.

Panel 43 (Reference Table BII) utilized Style 112 glass cloth with A-1100 finish. The glass was coated three times, each coating was dried 5 minutes @ 250°F providing a prepreg resin content of 74% w/w. Lap shear specimens provided a strength of 2000 psi which is noticeably better than unsupported adhesive strength values of 1000-1200 psi. Panel 46 (Table BII) was identical in construction to 43 except that it was autoclave cured for 1 hour @ 100 psi. The shear strength value is comparable to the press prepared panel (#43) except the larger standard deviation is probably a reflection of lower bonding pressures.

Since the BR-34 primer was not pre-cured in these supported adhesive studies, it was decided to try bonding under a lower pressure (50 psi) until 400°F was reached to permit volatile escape during P13N imidization prior to the application of 200 psi pressure at the final cure temperature. A lap shear value of 1990 psi for panel 47 provided comparable strength to that achieved through the normal pressure application methods of panel 46 and, therefore, offers no advantage. To determine whether the shear strength value was sensitive to cure time, panel 48 was prepared identical in construction to 47 except it was cured only 30 minutes compared to 60 minutes at 600°F. The shear strength value of 1920 psi compares favorably with 1990 psi indicating 30 minutes can be used as a cure time when tested at 75°F.

Burgman, et al (Reference 7) reported higher shear strengths when using 181 style glass compared to 112 style glass fabric as supports for polyimide adhesives. Panel 50 was prepared with 181 style glass to determine whether higher shear strength values could be obtained. The shear strength is lower than that obtained in panel 43, (Table BII), with 122 glass fabric A-1100 finish. In order to evaluate fully the shear strengths obtainable with the 181 glass fabric supported P13N adhesive, panel 55 was prepared with a double primer coat system. The first 40% w/w solids BR-34 (a revision of the originally used 27% w/w diluted BR-34) was cured followed by a knife coat application of 81% solids material dried for 30 minutes at 220°F. During press heat-up from 75°F, stepped pressure application of 50 psi to 475°F followed by 200 psi to 600°F where a cure time of 60 minutes was used. A shear strength value of 2528 psi was the highest value obtained for the P13N adhesive. To check reproducibility of this process, an identical panel

TABLE BII. SUMMARY OF TYPICAL SUPPORTED TITANIUM (6A1-4V) TENSILE LAP SHEAR STRENGTH DATA

Panel No.	PRIMER			ADHESIVE				TENSILE LAP SHEAR STRENGTH					
	System	Solids % w.w	Processed	System	Solids	Processed	CURING			No. of Test Specimens	R. T. psi	Standard Deviation psi	Type Failure % Surface Area
							Pressure psig	Temp. °F	Time Min.				
43	BR-34	81	30 Min. @ 220°F	Prepreg-P13N 112 glass A/1100 finish Resin Content-11%		3 coats each 5 min. @ 250°F	200	600	60	5	2000	49	A/G 100%
46	BR-34	81	30 Min. @ 220°F	Same as Panel	Number 43		100	55	60	5	1942	335	A/P-60 P/T-40
47	BR-34	81	30 Min. @ 220°F	Same as Panel	Number 43		30 200	400 400-600	60	5	1990	196	P/T-45
48	BR-34	81	30 Min. @ 220°F	Same as Panel	Number 43		200	600	30	5	1920	335	A/P-100
50	BR-34	81	30 Min. @ 220°F	Prepreg P13N 181 glass Z-6030 finish Resin Content 38%		3 coats each 5 min. @ 250°F	200	600	30	5	1296	157	A/P-20
53	None	--	---	Prepreg as Panel Number 50			200	600	30	5	637	136	A/T-100
55	BR-34	81	30 Min. @ 220°F	Same as Panel	Number 50		50 200	475 600	50	5	2528	332	A/P-100
	BR-34	81	15 Min. @ 550°F										
	BR-34	81	30 Min. @ 220°F										
60	BR-34	40	3 Coats each 10 Min. @ 220°F	Bloomingdale FM-34		As Received	200	550	30	5	3136	105	C/A-100
61	BR-34	40	30 Min. @ 220°F	Same as Panel	Number 50		50 200	475 600	60	5	2224	115	A/P-100
	BR-34	81	15 Min. @ 550°F										
	BR-34	81	30 Min. @ 220°F										

C/A - Cohesive failure of the adhesive

P/T - Primer to Titanium failure

A/T - Adhesive to titanium failure

A/P - Primer to Adhesive Failure

A/G - Adhesive to fiberglass support

61 was prepared a few days later which had a shear value of 2224 psi with a lower standard deviation.

Panel 53 was prepared without an adhesive primer to confirm the belief that P13N adhesive requires a primer. The shear value of 637 psi with a complete failure at the titanium/adhesive interface confirms this suspicion.

Panel 60 was prepared to determine whether the titanium pretreatment was satisfactory, whether dilution of the BR-34 primer to 40% solids with dimethyl formamide was detrimental, and to obtain some idea of the spread in data expected from FM-34 polyimide adhesive (a commercially available product). A tensile shear strength of 3136 psi with a standard deviation of 105 psi and a 100% cohesive failure shows the pretreatment is satisfactory, and dilution of the primer is not deleterious by comparison with published data for this system.

APPENDIX C

DETAILS OF PRIMER COMPOUNDING STUDIES

C.1 PRIMER BR-34 MODIFICATIONS

The first approach was to make additions of precursors for the TRW "A"-type polyamic acids to the BR-34 primer. Panels 85, 86 and 87 (Reference Table CI) were prepared by adding 5.0 pph of resin solids to the BR-34 primer of MPD, MA and BTDA respectively. The addition of MPD did not significantly improve shear strength as reflected by the primer to titanium failure at 1108 psi for Panel 85. The addition of NA in Panel No. 86 improved the shear strength to 1596 psi with failure occurring to the fiber glass support. Addition of BTDA slightly improved the shear strength and showed an adhesive to fiberglass failure (Panel 87). The addition of benzidine to BR-34 at 10 pph (Panel 103) did not significantly improve shear strength (1210 psi) although there was some improvement in adhesion to the metal. Based on these four panels, it was concluded that the anhydrides have more promise in overcoming the incompatibility problem than the diamines.

Because the addition of anhydrides to BR-34 provided improved compatibility (Panel 86 and 87), it was decided to investigate increased quantities of nadic anhydride. Panel 96 was prepared using 10 pph NA in BR-34. The first prime coat was cured at 600°F which then was overcoated with the same material and dried for 30 minutes at 220°F. The resulting strength was 2744 psi with good cohesive failure indicating that this level of NA is apparently required to obtain the required compatibility. An interesting and significant processing condition used to obtain these results was a pressure of 50 psi throughout the adhesive cure cycle. This indicates that this system may be suitable for autoclave bonding operations. Panels 99, 100 and 138 were prepared in an identical manner to 96 to demonstrate reproducibility. These panels provided room temperature shear strengths of 2600 psi initially and 2000 psi at room temperature after aging for 114 hours at 600°F. This compares favorably with commercially available polyimide adhesives which provide shear strengths in the range of 1900 psi when conditioned at 600°F in a similar manner.

TABLE CI. PRIMER STUDIES: SUMMARY OF BR-34 FORMULATIONS

Panel No.	Primer		Adhesive		Curing Pressure Psig	Room Temperature Lap Shear Tensile Strength, psi		
	System (2)	Processed	System (2)	Processed		Value (3)	Standard Deviation	Type Failure (1)
82	None	---	NA/MPD/BTDA Prepreg 181/ A1100	Resin Content-32% Volatiles-19%	200	702 [5]	78	A/T-100
84	NA/MPD/BTDA-100 Aluminum-175 Cab-O-Sil-5.0	Brush apply Dry 30' @ 220°F	Same as Panel 82		200	1054 [5]	276	P/T-100
108	P13N/108-100 Aluminum-175 Cab-O-Sil-5.0 A1100-1.5	Brush apply Dry 20' @ 220°F 10' @ 250, 300 350, 400°F Recoat and dry 30' @ 220°F	NA/MPD-SDA/BTDA prepreg 112/A-1100	Imidized 5' @ 250°F and 8' @ 350°F	50	929 [5]	84	P/T-100
109	NA/MPD/BTDA-100 Aluminum-175 Cab-O-Sil-5.0 A-1100-1.5	Same as Panel 108	Same as Panel 108		50	798 [5]	193	P/T-60
110	NA/MPD-SDA/BTDA filled as Panel 108	Same as Panel 108	Same as Panel 108		50	942 [5]	89	P/T-65
111	NA/MPD/BTDA-100 Aluminum-175 Cab-O-Sil-5.0 A-1100-1.5	Same as Panel 108	Same as Panel 108		50	1136 [5]	186	P/T-60
85	BR-34-100 (3) MPD-5.0 (2)	Knife coated and dry 30' @ 220°F	Same as Panel 82	Resin Content-32% Volatiles-19%	200	1108 [5]	106	P/T-100
86	BR-34-100 NA-5.0 (2)	Knife coated and cured 15' @ 250, 300, 350, 400, 450, 500, 550°F, recoat and dry 30' @ 220°F.	Same as Panel 82	Resin Content-39% Volatiles-12%	200	1596 [5]	105	A/G-70
87	BR-34-100 BTDA-5.0 (2)	Same as Panel 86	Same as Panel 82	Resin Content-39% Volatiles-12%	200	1297 [5]	151	A/G-70
103	BR-34-100 Benaldine-10	Brush apply Cure 30' @ 220°F, 10' @ 250, 300, 350, 400°F	Same as Panel 82	Resin Content-32% Volatiles-19%	50	1210 [5]	97	A/P&G-100
118	BR-34-100 PA-10	Knife coat and cure 30' @ 220°F and 10' @ 250, 300, 350 and 400°F	Same as Panel 108	Imidized 4' @ 350°F	50	135 [5]	57	P/T-100
119	BR-34-100 MA-10	Same as Panel 118	Same as Panel 118	Same as Panel 118	50	2576 [5]	68	C/A-100
96	BR-34-100 NA-10	Brush two coats dry 20' @ 220, 250, 275°F, 30' @ 300°F, 30' @ 600°F. Recoat and dry 30' @ @ 220°F.	Same as Panel 82		50	2744 [5]	108	C/A-100
99 and 100	BR-34-100 NA-10	Same as Panel 96	Same as Panel 82		50	2644 [5] 1965 (4)	165 143	C/A-100 C/A-100
101	BR-34-100 NA-10 DMF-635	Brush coat Cured 30' @ 220 and 550°F, Recoated with 70% solids BR-34	Same as Panel 82		50	1799	190.9	A/P-100
105	BR-34-100 NA-10	Brush coat Cured 30' @ 220°F and 10' @ 250, 300, 350, 400°F, Re- coat and dry 20' @ 220°F.	NA/MPD-SDA/ BTDA Prepreg 112/A-1100	Resin Content-64% Volatiles-26%	50	2792 [5]	107	C/A-100
106	BR-34-100 NA-10	Same as Panel 105	NA/MPD/BTDA Prepreg 112/A-1100	Resin Content-59% Volatiles-20%	50	2770 [5]	214	C/A-100
138	BR-34-100 NA-10	Same as Panel 105	Same as Panel 106		50	2960 2173 (4)	56 122	C/A-100

(1) Type failures: C/A - Cohesive of adhesive; A/T - adhesive to Titanium; P/T - primer to Titanium
A/G - adhesive to fiberglass support.

(2) MPD - metaphenylene diamine; NA - nadic anhydride; BTDA - benzophenone tetracarboxylic acid dianhydride
MA - maleic anhydride; PA - phthalic anhydride; TMA - trimellitic anhydride; MDA - methylene dianiline.

(3) [] number of test specimens.

(4) Tested at R. T. after 100 hours @ 600°F.

Because blistering was encountered while preparing Panel 96, a primer was prepared at 10% resin solids and used to prepare Panel No. 101. Despite the fact this panel was prepared similar to 96, the shear value dropped to 1800 psi with a primer to adhesive failure which indicates the primer-coat thickness is critical.

Summation of the BR-34 modifications studies are as follows:

- The proprietary primer BR-34 can be made to be more effective with TRW's "A"-type polymers by the addition of 10 pph of nadic anhydride
- The modified BR-34 primer has provided good cohesive failures at satisfactory stress levels using a bonding pressure of only 50 psi.

C.2 EVALUATION OF TRW "A"-TYPE POLYIMIDES BLENDED WITH AMIDE-IMIDE RESINS

In the course of evaluating proprietary materials as candidate primers, Amoco Chemical Company's polyimide-imide AI-1137 resin was investigated. The first evaluation of the material as a primer was performed on Panel 117 (Table CII) which failed as a result of insufficient primer. The same primer system then was used in combination with aluminum filled AI-1137 adhesive in Panel 123 which provided the best room temperature shear strength values to date on this program (5000 psi). After 100 hours exposure at 600°F in air, the shear strength value at room temperature was 3260 psi. The aluminum filled AI-1137 was used as a primer in Panel 124 which provided equivalent room temperature shear strength and improved strength retention after 100 hours at 600°F.

Published data on the AI-1137 resin system shows that strength retention at temperatures over 500°F is very low therefore it was decided to determine whether the TRW "A"-type polyimide resins would upgrade the AI-1137 resin when both were used as an integrated system. A control panel (137) was prepared using 100 parts of AI-1137 filled with 100 parts of atomized aluminum which provided good room temperature values; however, when tested at 600°F after a 10 minute soak, the shear strength was only 200 psi. The addition of 25, 50 and 75 parts by wt of NA/MDA/BTDA per 100 parts of total resin solids in panels 127, 129 and 128 respectively, provided shear

TABLE CII. PRIMER STUDIES: SUMMARY OF AMIDE-IMIDE FORMULATIONS

Panel No.	Primer		Adhesive		Curing (4)		Pre-Aging Lap Shear Strength, psi			Lap Shear Strength After 1000 Hours @ 600°F, psi		
	System (2)	Processed	System (2)	Processed	Temp. °F	Time Mins	Value (3)	Std. Deviation	Type Failure %	Value	Std. Deviation	Type Failure % (1)
117	AI-1137-10(5) MNP Solvent-90	15' @ 275°F	NA/MPD-SDA/ BTDA Prepreg 112/A-1100	Resin Content-64% Volatiles-26%	600	30	759 [5]	108	A/P	--	---	---
123	Same as Panel 117		AI-1137-100 Aluminum-100	15' @ 275°F and 5' @ 350°F	550	60	5000 [2]	--	C/A-100	3266 [3]	358	C/A-100
124	AI-1137-100 Aluminum-100	15' @ 275°F 5' @ 350°F	Same as Panel 117		550	60	5050 [3]	763	C/A-100	4380 [2]	28	C/A-100
127	None		AI-1137-75.0 NA/MPD/BTDA- 25.0 Aluminum-100 Cab-O-Sil- 5.0	15' @ 275°F 5' @ 350°F	550	60	3880 [2]	56.6	C/A-100	721 [3]	34	C/A-100
128	None		AI-1137-25.0 NA/MPD/BTDA- 75.0 Aluminum-100 Cab-O-Sil- 15.0	Same as Panel 127	550	60	987 [2]	94.7	A/P-75	1154 [3]	81.5	A/T-80
129	None		AI-1137-50 NA/MPD-SDA/ BTDA-50.0 Aluminum- 100 Cab-O-Sil- 10.0	Same as Panel 127	550	60	2020 [2]		A/T-75	1363 [3]		A/T-35
134	None		AI-1037-100 Aluminum- 100	15' @ 275°F 5' @ 350°F	550	60	5290 [2]	99	C/A-100	199 [3]	192	C/A-100
137	AI-1137-50.0 NA/MPD/BTDA- 50.0 Aluminum- 100.	15' @ 275°F 5' @ 350°F	Prepreg 112 glass AI-1137- 50.0 NA/MPD/BTDA- 50.0	Resin Solids-82% Volatiles-39%	550	60	3620 [2]	254	C/A-100	2786 [3]	35	A/P-75
141 & 142	AI-1137-25.0 NA/MPD/BTDA- 75.0 Aluminum- 100.	15' @ 275°F 5' @ 350°F	Prepreg 112 glass A-1100 with AI-1137-25.0 NA/MPD/BTDA- 75.0	Resin Solids-74% Volatiles-19%	600	30	1190 [5]	175	P/T-100	1400 [5]	74	A/P-100
145	AI-1137-50. NA/MPD/BTDA-50. Aluminum-100. Cab-O-Sil-5.0	15' @ 275°F 5' @ 350°F	Same as Panel 137		550	60	3210 [2]	42.4	A/P-100	2546 [3]	100.6	C/A-100
146	AI-1137-25.0 NA/MPD/BTDA- 75.0 Aluminum- 100. Cab-O-Sil- 5.0	15' @ 275°F 5' @ 350°F	Same as Panel 141-2		550	60	1221 [2]	57.9	A/P-100	1488 [3]	39	C/A-100
150	Same as Panel 137		AI-1137-50. NA/MPD/BTDA- 50.0 Aluminum- 175.0 Cab-O-Sil- 5.0	15' @ 275°F 5' @ 350°F	550	60	3440 [2]	56.6	C/A-100	2550 [3]	118	C/A-100

(1) Type failures: C/A - Cohesive of adhesive; A/T - adhesive to Titanium; P/T - primer to Titanium;
A/G - adhesive to fiberglass support.

(2) MPD - metaphenylene diamine; NA-nadic anhydride; BTDA - benzophenone tetracarboxylic acid dianhydride
MA - maleic anhydride; PA - phthalic anhydride; TMA - trimellitic anhydride; MDA - methylene dianiline.

(3) [] number of test specimens.

(4) Tested at R. T. after 100 hours @ 600°F.

strengths at 600°F after the 10 minute soak of 721, 1363 and 1154 psi respectively. In an effort to improve the R.T. shear strength of the resin system containing equal amounts of TRW polyimide and AI-1137, the resin was used on a 112 glass carrier. Panels 137, 150 and 145 all substantiate that a 50/50 mixture of AI-1137 and NA/BTDA/MPD will provide a room temperature shear value of 3400 psi, and 2600 psi after 100 hours at 600°F. Using the value of 3400 psi as an expected room temperature shear strength for the 50/50 mixture resin system, and the percent strength retention of 67.2% at 600°F (panel 129, 1363 psi from 2020 psi), one can project an anticipated shear strength value for the 50/50 resin system of 2280 psi (0.67×3400 psi) rather than the 1363 actually obtained. This compares quite favorably with reported values (Reference 8) of 1800 psi for FM-34 adhesive using Titanium 6Al-4V alloy.

Additional panels were prepared using a 25/75 ratio of these resins as a primer which provided a room temperature shear strength value of 987 psi and 1154 psi at 600°F. Panels 141 and 142 were prepared using the same primer without Cab-O-Sil and with a supported 25/75 adhesive mixture. The room temperature shear strength value of 1190 psi confirms values from panel number 128 but also shows that supporting the adhesive has little effect on room temperature shear strength.

Panel 146 which is essentially the same as 141 and 142 with the addition of 5.0 pph Cab-O-Sil in the primer had an equivalent room temperature shear strength of 1221 psi. All of these panels had a slight increase in shear strength after aging at 600°F and testing at room temperature. This is quite common with many polyimide systems.

It was concluded from these studies that both the polyamide-imide polymer either alone or in a 50/50 combination with TRW resin NA/BTDA/MPD have definite promise as high temperature primer systems for the TRW "A"-type polyimide adhesive compounds.

C.3 EVALUATION OF COMMERCIALY AVAILABLE HIGH SERVICE TEMPERATURE PRIMERS

Several commercially available high service temperature adhesive primers and coatings were procured and evaluated. DuPont PI-4701 was evaluated in Panel 89 (Table CIII) by itself and with NA added in Panel 102 but both tests demonstrated poor adhesion to titanium. DuPont PI-5510 adhesive primer was evaluated with DuPont 5505 polyimide prepreg (Panel 139)

TABLE CIII. PRIMER STUDIES: SUMMARY OF CANDIDATE PROPRIETARY PRIMERS

Panel No.	Primer		Adhesive		Curing			Tensile Lap Shear strength		
	System	Processed	System	Processed	Pressure psig	Temp. °F	Time Min.	R. T. psi (*)	Std. Deviation psi	Type Failure %
89	DuPont and Co. PI-4701-100.0 DMF-10.0	Brush apply Dry 30' @ 220°F	NA/MPD/BTDA Prepreg 181/A-1100	Resin Content-32% Volatiles-19%	200	600	30	557 (5)	68	P/T-100
102	PI-4701-100.0 NA-10.0	Brush apply Dry 30' @ 220°F and 10' @ 250, 300, 350, 400, 450, 500, 550°F	Same as Panel 89		50	600	30	1200 (5)	76	P/T-100
116	DuPont and Co. PI-5510	20' @ 250°F	NA/MPD-SDA/BTDA Prepreg 112/A-1100	Resin Content-64% Volatiles-26%	50	600	30	1175 (5)	72	P/T-100
139	None		DuPont & Co. PI-5510	20' @ 250°F	30 30 30	350°F 500°F Cool to 250°F	10 60 Post Cure 42 hours @ 600°F	1259 (2) 1257** (3)	126 109	P/T-80 A/T-100
143	Westinghouse Omega Enamel B-519	10' @ 275°F	None		50	600	30	2060 (5)	99	C/A-100
152	Minnesota Mining Mfg. Co. EC-2333	30' @ R. T. & 30' @ 160°F	NA/MPD/BTDA Prepreg 112/A-1100	Resin Content-60% Volatiles-20%	50	600	30	735		A/P-100

P/T - Primer to Titanium failure

A/T - Adhesive to titanium failure

C/A - Cohesive failure of the adhesive

A/P - Primer to adhesive failure

**Tested at 600°F after 10 mins soak.

*Number of specimens

TABLE CIV. PRIMER STUDIES: SPECIALTY POLYMERS

Panel No.	Primer		Adhesive		Tensile Lap Shear Strength					
	System	Processed	System	Processed	R. T. psi (*)	Std. Deviation psi	Type Failure %	R. T. After 100 hr. Aging At 600°F psi	Std. Deviation psi	Type Failure %
144	50NA:50TMA/MPD/ BTDA 100.0 Aluminum 100.0 Cab-O-Sil 5.0	20' @ 250°F	NA/MPD/BTDA Prepreg 112/A 1100	Resin Content-60% Volatile-20%	1004 (2)	108	A/G-100	802	137	A/G-100
147	Same as 144	20' @ 250°F +8' @ 350°F	Same as panel 144	8' @ 350°F	1160 (2)	141	P/T-60	1171 (3)	143	A/P-100
148	Same as 147	Same as 147	MNTB Prepreg 112/A1100		1040 (2)	28	P/T-75	1271 (3)	159	A/P-100
133	Aluminum 175 Nadic Anhydride 10.0 Cab-O-Sil 10.0 MDA/BTDA 100.0	30' @ 220°F	NA/MPD-SDA/BTDA Prepreg 112/A1100	Resin Content-64% Volatile-26%	1376	235	C/P-85	---	---	---

A/G - Adhesive to fiberglass support

A/P - Primer to adhesive failure

*Number of specimens.

and with TRW NA/BTDA/MPD (Panel 116) but poor adhesion to titanium was observed in both cases.

A material designated as B519 Omega Class H single film polyester-amide-imide enamel from Westinghouse Electric Corporation was evaluated as a candidate primer in Panel 143. Two coats of the enamel were dried at 275°F and the adhesive was cured per Table CIV. The room temperature shear strength values were reasonable considering that a thin glue line was obtained. The glue line was charred indicating the material would probably not withstand continuous 600°F service. The fact that it contains cresylic acid as a solvent also indicates potential corrosion problems, and no further work with the compound was performed.

One other primer, EC-2333 from the Minnesota Mining and Manufacturing Company, was evaluated. This is classified as a silane type and has previously been evaluated in the polyimide adhesive study reported by J. Mahon (Reference 4). When used in conjunction with TRW NA/MPD/BTDA adhesive prepreg (Panel 152) low shear strength values were obtained.

It was concluded from the above properties that the commercially available primers evaluated in these studies were not suitable for further evaluation during this program.

C.4 EVALUATION OF SPECIALLY SYNTHESIZED TRW POLYMERS

Evaluation of commercially available resins and primers indicated that long chain polyimide polymers (BR-34) or pendant carboxy and amide groups (AI-1137) provided better adhesion to titanium alloy than obtained with the TRW "A"-type polyimides. Therefore, it was decided to synthesize special polyimide polymers that would provide improved adhesion by one of the above mechanisms. The first polymer prepared was formulated with BTDA and MDA at a 1100 FMW. Nadic anhydride was added to the resultant amic acid in the same manner as for the BR-34 primer. A panel bonded with TRW NA/MPD/BTDA adhesive prepreg (Panel 133) did not provide good shear strength values.

The second polymer prepared consisted of trimellitic anhydride as a substitute of one-half the stoichiometric amount of nadic anhydride in the standard NA/MPD/BTDA formulation. Panels 141, 144 and 148 were prepared

using this system but significant improvement in shear strength values were not obtained.

APPENDIX D.

PREPARATION OF BORON COMPOSITE, LAP SHEAR AND SHORT BEAM SHEAR SPECIMENS

D.1 PREPARATION OF BORON/POLYIMIDE PREPREG AND COMPOSITES

Boron polyimide prepregs were drum wound using United Aircraft 0.004-inch diameter boron monofilament, TRW P13N polyimide resin and style 104-A1100 glass scrim cloth. The boron mono-filament used throughout this program was substandard grade because materials meeting standard USAF requirements were not available within a reasonable delivery schedule. Comparison between the properties required by USAF and of the procured material are as follows:

	<u>USAF Rgt.</u>	<u>Procured Material</u>
Length of filament on spool feet	35,000	35,000
Tensile strength, min. ave Ksi	400	335 to 399
% strength deviation allowable below min. ave.	20	See above
Fiber dia. inches	0.0037 to 0.0041	0.0037 to 0.0041

It was mutually agreed by the NASA and TRW program managers that, because shear failures in short beam specimens usually occur at a load much lower than that required to fail the fiber in tension, the lower quality boron filament was acceptable.

TRW P13N resin was used as a matrix for the filaments rather than the NA/MPD/BTDA resin (as used in the adhesive) because preliminary fabrication studies had indicated that different processing was required. Processing of P13N had been established prior to commencing this program and since the prime purpose of this program was to develop polyimide adhesives rather than boron polyimide composites, developmental efforts with the NA/MPD/BTDA system were not instigated.

The P13N/boron prepregs consisted of 208 filaments/inch at a resin content of 40 to 50 percent by weight and had a volatiles content of 12 to 18 percent by weight. Molding of these composites proceeded by stacking 0.25-inch wide strips of prepreg to twelve plies thickness in the cold nine cavity mold (Figure 12). The mold then was assembled and placed into a 400°F air circulating oven for two hours. After this cycle (imidizing cycle) the

hot mold was removed from the oven and placed into a press preheated to 600°F. Immediately, pressure was applied to the mold until it was fully closed to stops whereupon the composites were cured under pressure for one hour. The resultant composites were nine-inch long by 0.258-inch wide by 0.065-inch thick. Flexural moduli of these composites were 27×10^6 psi at room temperature and 20×10^6 psi at 600°F. Resin content of the composites was 21% w/w. Previous experience by TRW Systems in evaluating P13N boron filament composites has provided flexural moduli of 30×10^6 psi. The lower modulus of 27×10^6 psi at room temperature obtained with the composites in this program is attributed to the lower quality boron mono-filament utilized for these studies.

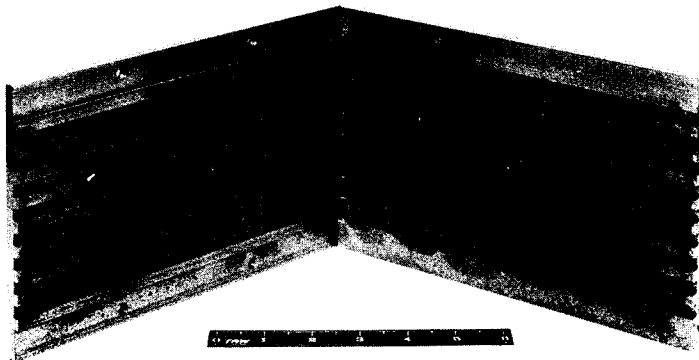


Figure 12. Photograph of Nine Cavity Mold

D.2 PREPARATION OF LAP SHEAR TEST SPECIMENS

The titanium 6Al-4V faying surfaces of the lap-shear finger test panels were vapor degreased, grit blasted with 50 micron alumina and water rinsed. They then were immersed in Pasa Jel 107 for 15 minutes at 70°F, water rinsed and dried at 150°F. All panels were primed within two hours of preparation. The primer was thinly applied by brush and then dried in an air circulating oven for 15 minutes at 275°F and imidized by thermal treatment for 5 minutes at 350°F. Paste adhesive was splined onto the primed surfaces, then dried and imidized by the same process as used for the primer, after which the faying surfaces were mated and the specimens were assembled in the lap-shear bonding jig. These assemblies then were cured in a press under 150 psig pressure at 550°F for one hour.

D.3 PREPARATION OF PRIMARY BONDED SHORT BEAM ASSEMBLIES

Titanium alloy 6Al-4V faying surfaces were prepared and primed in the same manner as the lap shear test specimens. P13N/boron prepreg cut into 0.25-inch wide strips were stacked twelve plies thick in the nine cavity mold. After assembling the mold, it was placed into a 400°F air circulating oven for two hours. The primed titanium alloy strips were located on top of the imidized P13N/boron prepreg and the hot mold then was transferred to a press preheated to 550°F and pressure was applied immediately to fully close the mold to stops. Cure cycle for these assemblies was one hour at 550°F.

D.4 PREPARATION OF SECONDARY BONDED SHORT BEAM ASSEMBLIES

Titanium alloy 6Al-4V faying surfaces were prepared and primed in the same manner as the lap shear test specimens. P13N/boron composite faying surfaces were prepared by lightly abrading the boron face with 320 grit silicon carbide paper and washing with acetone. These surfaces then were primed by the same process as for the titanium alloy specimens. Paste adhesive was applied to the primed surfaces and thermally treated for 20 minutes at 275°F and 5 minutes at 350°F. The faying surfaces then were mated and the assemblies were placed into the cold nine cavity mold (as used for molding the composites). These assemblies were cured in a press at 550°F for 60 minutes under sufficient pressure to keep the mold fully closed to stops (spacers were used to compensate for the increased thickness of the bonded assemblies over the composites).

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